

THE
STABILITY OF GYPSUM AND ANHYDRITE
IN
THE GEOLOGIC ENVIRONMENT

by
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(1950)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF
DOCTOR OF PHILOSOPHY
at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September, 1954

Signature of Author.....

Department of Geology and Geophysics, September 10, 1954

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In the $\text{CaSO}_4\text{—H}_2\text{O}$ system, gypsum and anhydrite are the only two minerals that are sufficiently stable to exist as geologic deposits. From thermodynamic data and solubility measurements the transition temperature has previously been found to be about 40°C , above which anhydrite is the stable phase and below which gypsum is the stable phase, when they are in contact with an aqueous solution at atmospheric pressure. By a process of solution and recrystallization, one can be converted to the other, after the surrounding liquid is saturated with calcium sulphate. Experimental work has been done in a study of the effects of pressure on this transition point, and the results corroborate and extend the theoretical calculations of MacDonald, which are based on thermodynamic data. This experimentally determined information was used in explaining some of the gypsum-anhydrite sequences found in geologic deposits.

The experiments were conducted using high pressure bombs which contained samples of pure gypsum or anhydrite in a saturated calcium sulphate solution. By placing these bombs in electric furnaces and allowing sufficient time for equilibrium to be reached, the more stable mineral would recrystallize out of solution. Anhydrite thus formed in original gypsum could be detected under a microscope, whereas gypsum formed from original anhydrite could be distinguished by differential thermal analysis. These determinations were conducted in groups at pressures of 250, 500, 1000, 1500, and 2000 atmospheres, and the transition temperatures were found to be approximately 43° , 46° , 53° , 62° , and 74°C respectively. These are for equal lithostatic and hydrostatic pressures. A new phase in the $\text{CaSO}_4\text{—H}_2\text{O}$ system is believed to be formed at 2000 atmospheres, as indicated by an endothermic peak at 270°C on thermograms of original anhydrite partially converted to gypsum.

The cryohydric point in the $\text{CaSO}_4\text{—H}_2\text{O}$ system was found by direct experiment to be -0.7°C .

Differential thermal analyses of a number of Nova Scotia gypsum samples were found to be identical, within the limits of experimental error, and therefore could not be used as a means of correlating gypsum beds in different localities.

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INTRODUCTION

There are a number of problems connected with the study of geologic deposits of gypsum and anhydrite, some of which are completely unsolved and open to speculation. As evaporite minerals, they have been precipitated from evaporating bodies of water, the latter usually having had some direct or indirect connection with the sea at one time. It would seem an easy matter to reproduce similar deposits on a laboratory scale, but the difficulties encountered only help point out the complexity of the problem, for there are many unknown factors which can only be assumed. Conversely, there are many known facts concerning the present deposits of calcium sulphate that cannot be fully explained or accounted for unless the assumptions made as to geologic conditions are so limited as to make them untenable.

The geologic problems brought up by these particular evaporite deposits can be placed into three categories: (1) when were they deposited; (2) how were they deposited; and (3) what transformations have they undergone since their original deposition. The first problem can usually be solved by looking outside the deposits themselves and examining the surrounding structural and stratigraphic conditions, since fossils as age markers within massive gypsum and anhydrite beds are often rare. As to how they were deposited, there are well established theories, such as the Bar Theory of

Ochsenius and its modifications, as well as experimental data (some of it conflicting), which try to account for the details of precipitation. This will be discussed later. Less is known about the problem of post-depositional changes once the gypsum and anhydrite have been formed into deposits. Except for the work of Griggs,²³ no experimental data on the effects of pressure have heretofore been available or used to fit in with the other factors of temperature and solution effects to get an overall picture of the conditions imposed on buried calcium sulphate deposits.

The main contribution of this present investigation is to add some further information to that already known about the effects of pressure and temperature on gypsum and anhydrite in contact with an aqueous solution. Experiments have been conducted, with some success, in which saturated calcium sulphate solutions containing solid particles of gypsum or anhydrite have been put under a hydrostatic pressure at a specified temperature and allowed to approach equilibrium. If they were originally stable at that pressure and temperature, no change would be noted aside from solution or recrystallization effects. However, if one or the other was unstable it would go into solution and recrystallize out as the more stable phase. From previous work it is known that of all the possible calcium sulphate minerals only gypsum and anhydrite are completely stable in an aqueous solution and therefore, this investigation has experimentally

determined the transition line separating the two regions of their respective stabilities. This is an important step in the study of gypsum and anhydrite beds, for if estimates of the depth of burial, temperature, and concentration of ground water solutions can be made for these deposits then the stable calcium sulphate phase can be determined.

Finally, in an attempt to find some means of correlating gypsum and anhydrite zones, a number of differential thermal analyses were made of selected samples. This investigation had negative results, since all the thermograms of gypsum and anhydrite proved to be extremely similar, respectively, indicating constant, or almost constant compositions of the analyzed materials.

CHAPTER I

PREVIOUS WORK

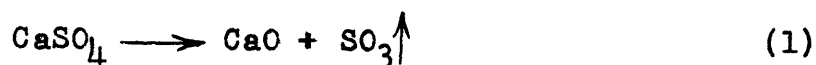
EARLY WORK

Gypsum has always ranked as one of the more abundant and useful non-metallic mineral deposits. As early as 1765, Antoine Laurent Lavoisier published a paper³² on his experimental study of gypsum and its dehydration products in which he reported: "If gypsum, which has been deprived of its water of crystallization by means of heat, is again treated with water, it takes it up with avidity, a rapid and irregular crystallization occurs, and the small crystals which are formed are so entangled in each other that a very hard mass results." He also observed³³ that when gypsum dehydrates, it does so in two stages. The first portion of water (75% of the total) is driven off more easily than the remaining 25%.

LeChatelier³⁴ was the first to determine the decomposition temperature of this reaction. He did this by placing gypsum in a glass tube immersed in a paraffin bath and slowly heating the latter while recording the temperature of the gypsum by means of a thermometer. At 128°C and at 168°C there were breaks in the otherwise even rise of temperature, indicating that heat was being absorbed and an endothermic reaction was occurring.

COMPOSITION AND PHASE RELATIONS

Gypsum is composed of calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and has the very useful property of being converted to the hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), commonly known as Plaster of Paris, upon heating in air to about 128°C . Continued heating will cause the hemihydrate to lose its half molecule of water at about 163°C ²⁶ where it becomes soluble anhydrite (CaSO_4). At about 370°C this is converted to the insoluble anhydrite (CaSO_4), a polymorph of the soluble anhydrite. Continued heating above this temperature will produce no change until 1193°C is reached where a high temperature form of anhydrite appears. At 1250°C dissociation occurs and the CaSO_4 is partially broken down to its constituents according to the following chemical equation:⁵²



There are two forms of the hemihydrate, an α and a β form, and corresponding α and β forms of the soluble anhydrite. The insoluble anhydrite is often referred to as the γ form. A point to be made here that may avoid confusion later is that Posnjak⁴⁴ proposes the soluble anhydrite to be known as γ -anhydrite, the insoluble anhydrite to be called β -anhydrite, and the high temperature form as α -anhydrite (after an enantiotropic inversion takes place at about 1193°C forming triclinic crystals). Kelley et al³⁰ uses these terms quite differently, and his notation seems

to have been more widely accepted. The α - and β - designations are used only as prefixes in describing any variations in one form, such as α - and β - hemihydrate, etc. Both notations are found in the literature, however, and it is important to be sure which one the author is using. Kelley's notation is preferred here, and is used throughout this paper.

Until fairly recently it was often thought that the water contained in or associated with calcium sulphate was not the same as the water of crystallization found in other hydrated minerals but was rather more like the water contained in the hydrous silicates known as zeolites. Here the water is not a very important part of the crystal structure but is believed to be adsorbed. Upon heating it can be driven off in a continuous manner. Thus, it was thought that the amount of bound water associated with the calcium sulphate could continuously vary from none in pure anhydrite to two molecules in pure gypsum. According to Wyckoff⁶⁰ from x-ray analysis, "a completely satisfying interpretation is made difficult by the fact that the hemihydrate and a completely dehydrated product yield the same pattern. From this it has been concluded that the water is zeolitic in the sense of being haphazardly distributed throughout the structure."

Today, it is generally agreed that only the forms containing two molecules ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), one half molecule

($\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$), or no molecules (CaSO_4) of water can exist, either in nature or in the laboratory. All the experimental and field observations by the author substantiate this viewpoint and later in this paper there will be a discussion of some analyses of so-called "water-short gypsum" samples.

Kelley, Southard, and Anderson³⁰ in 1941 did experimental work to clarify and add to the data on gypsum and its dehydration products. They obtained heats of hydration, both directly and indirectly, low temperature specific heats, and dissociation pressures of the dihydrate, the two hemihydrates, the two soluble anhydrites, and the insoluble anhydrite. Before their work established a limit on the known number of gypsum and its dehydration compounds it was thought that there were two types of the dihydrate, at least three of the hemihydrate, and at least four of the anhydrite, although diffraction-powder photographs could not identify them as separate compounds. They found that gypsum, whether artificially precipitated at room temperature, or found in nature as large transparent crystals of selenite or as fine grained compact masses of small crystals, always had the same energy content and "probably had the same crystal form." The latter was believed to be monoclinic prismatic in form with four or eight molecules in a unit cell. The "crystal lattice is made up of layers of calcium atoms and sulfate groups separated by sheets of water molecules," the latter

forming an important part of the crystal structure. If the water is removed it would alter this structure. These sheets of water molecules account for the excellent cleavage that is found in selenite.

For the hemihydrate, Kelley describes Gallitelli's findings in 1933 of the structure as a "deformed monoclinic structure with 12 molecules of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ in a unit cell. The lattice possesses great stability because the calcium atoms and sulfate tetrahedrons are arranged in such a way that there are strong forces between the calcium atoms of one layer and the SO_4 groups of the adjacent one. However, channels in which the water molecules are situated exist in the lattice. The forces between the water molecules in these channels and the calcium atoms and sulfate groups are weaker than between the last two because relatively greater distances are involved, which apparently permits at least part of the water to be removed without seriously disrupting the structure of the crystal--the opposite of what happens in the case of the dihydrate." Thus, to a certain extent, the hemihydrate may be considered zeolitic. Kelley concludes that there are but two hemihydrates, an α -hemihydrate and a β -hemihydrate. The latter has a higher energy content and a higher solubility and is therefore less stable, but apparently the two cannot be distinguished by x-ray powder-diffraction patterns. The α -type is considered stable and the β -type metastable in relation to each other.

AFTER KELLEY ET AL.

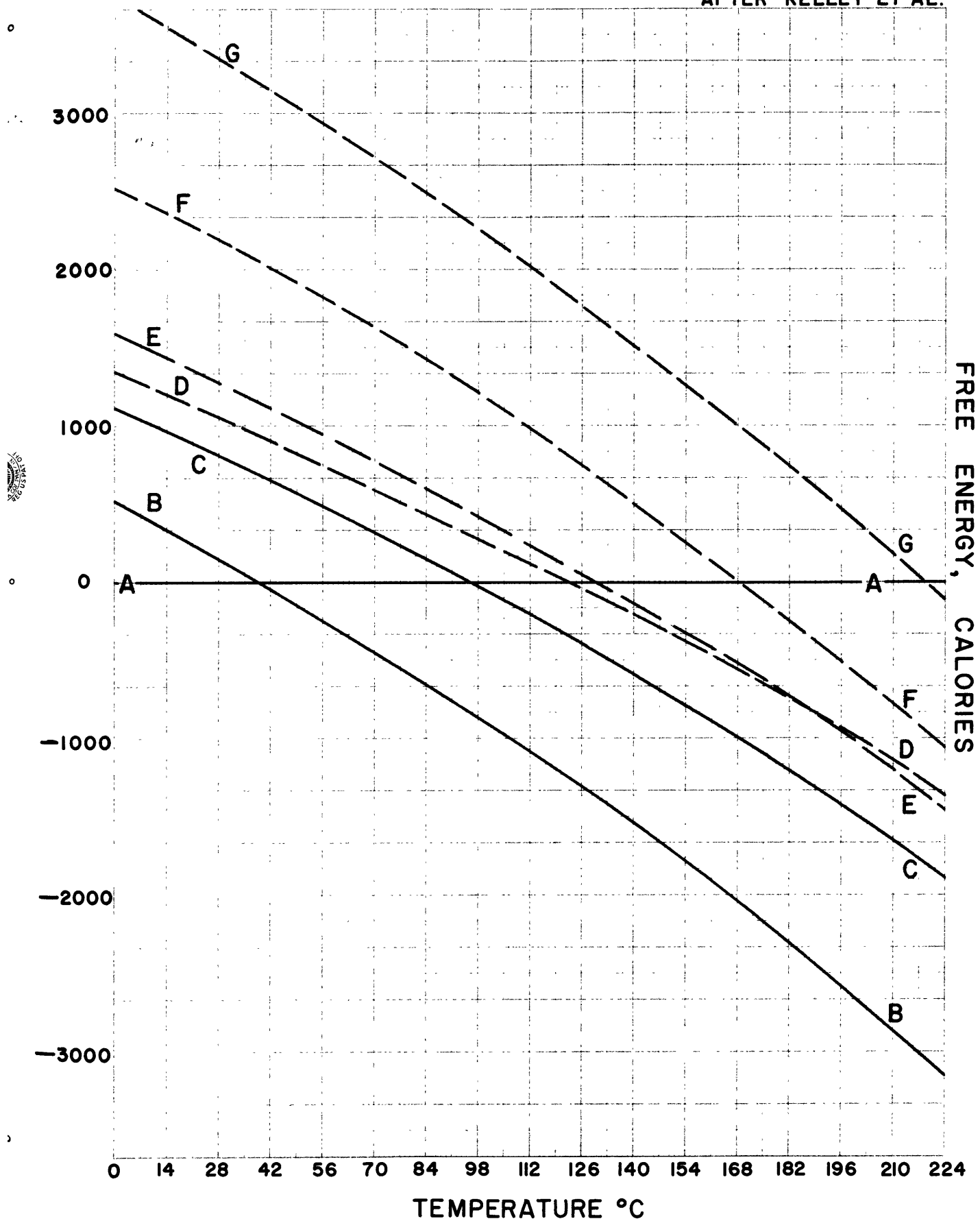


FIGURE I.

According to Kelley, the α -hemihydrate "may be prepared from the dihydrate in the presence of liquid water above 97°C or in a steam-saturated atmosphere. It loses water in one step and is to be considered non-zeolitic.

β -hemihydrate may be prepared from the dihydrate by dissociation in a vacuum or in a nearly dry atmosphere followed by annealing at about 100°C . It loses water with the formation of a soluble anhydrite containing several tenths percent water. From 0.9 percent water down the water is removed with increasing difficulty, hence this part may be considered zeolitic if desired." It is to be noted here that although Kelley uses the terms stable and metastable for the hemihydrate, he also clearly indicates that there are only two completely stable substances in the $\text{CaSO}_4\text{---H}_2\text{O}$ system, and these are the dihydrate and the insoluble anhydrite, that is, the gypsum and anhydrite that occur in the geologic environment. Figure 1 is a free-energy diagram, after Kelley, that shows the free energy changes that occur when $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is dissociated into the two hemihydrates, the two soluble anhydrites, and the insoluble anhydrite. A curve for the breakdown to $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} (\alpha)^*$ is also included, the asterisk representing "material having a greater, but unknown amount of water than is indicated." Curve B-B is the free energy of the reaction for the breakdown of gypsum to the insoluble anhydrite plus water; Curve C-C is for the breakdown of gypsum to $(\alpha)^*$ -hemihydrate; Curve D-D

DATA FROM INTERNATIONAL CRITICAL TABLES

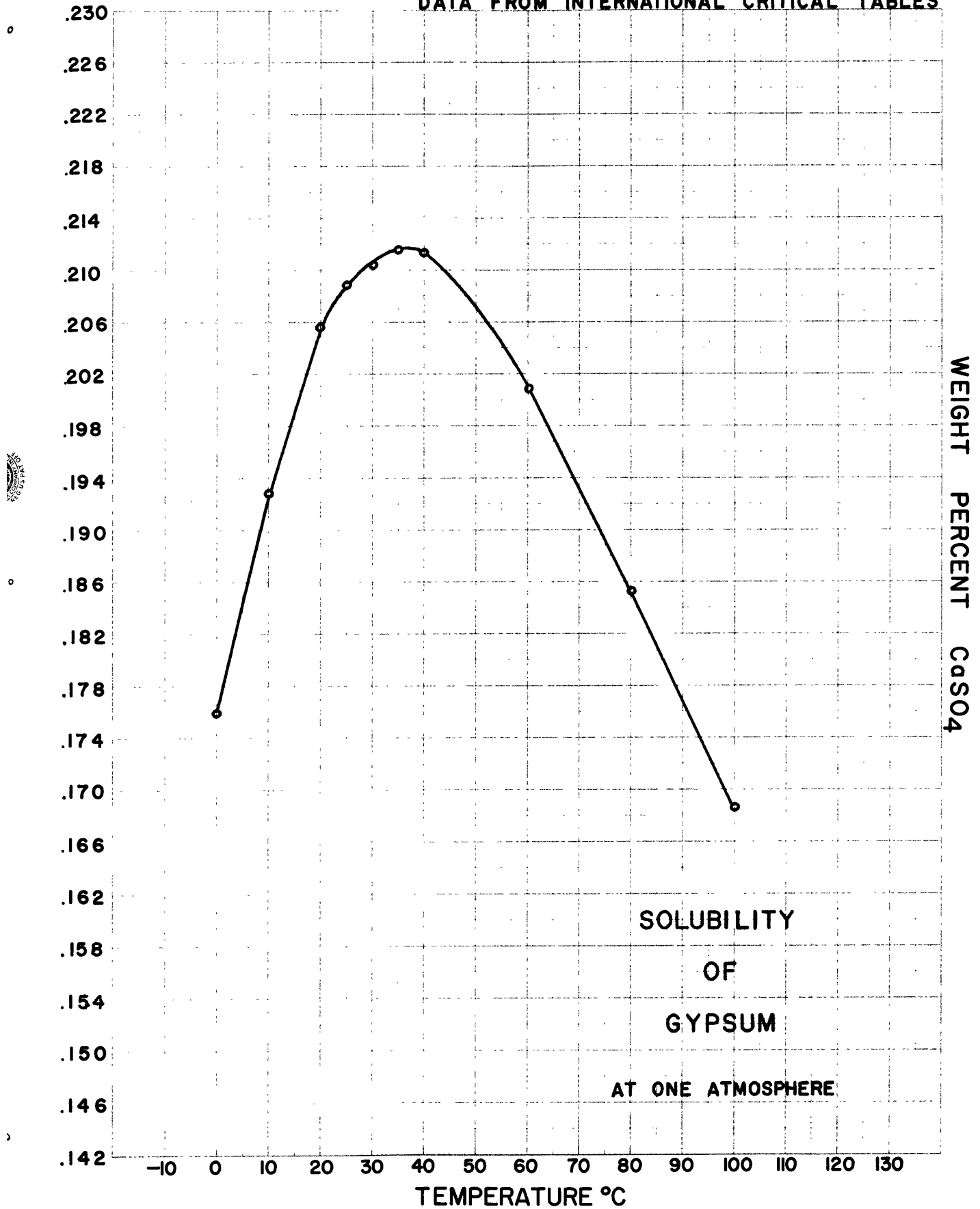


FIGURE 2.

is for the breakdown of gypsum to α -hemihydrate; Curve E-E is for the breakdown of gypsum to β -hemihydrate; Curve F-F is for the breakdown of gypsum to the soluble α -anhydrite; Curve G-G is for the breakdown of gypsum to the soluble β -anhydrite. Since a measure of stability is the amount of free energy of a reaction, with the more stable substances having the lowest free energy, the diagram shows that only gypsum and the insoluble anhydrite are stable.

The crystal structure of insoluble anhydrite has a simple orthorhombic lattice with a unit cell of four molecules. Its lattice has the closest packing, the highest density, and the most stable arrangement of any of the calcium sulphates, which accounts for its low reactivity. Whether found naturally or produced artificially, its optical and thermal properties are the same.

SOLUBILITY

The solubility of gypsum in pure water is very low and is different from most other salts in that it exhibits retrograde solubility. From 0°C to higher temperatures its solubility slowly increases until at about 40°C it reaches a maximum. From here to 100°C it gradually becomes less soluble. Figure 2 is a solubility diagram of gypsum²⁹ and it clearly illustrates the broad peak of maximum solubility. Figure 3 is a similar diagram showing the solubility of anhydrite³⁰ over the same temperature range. In contrast to

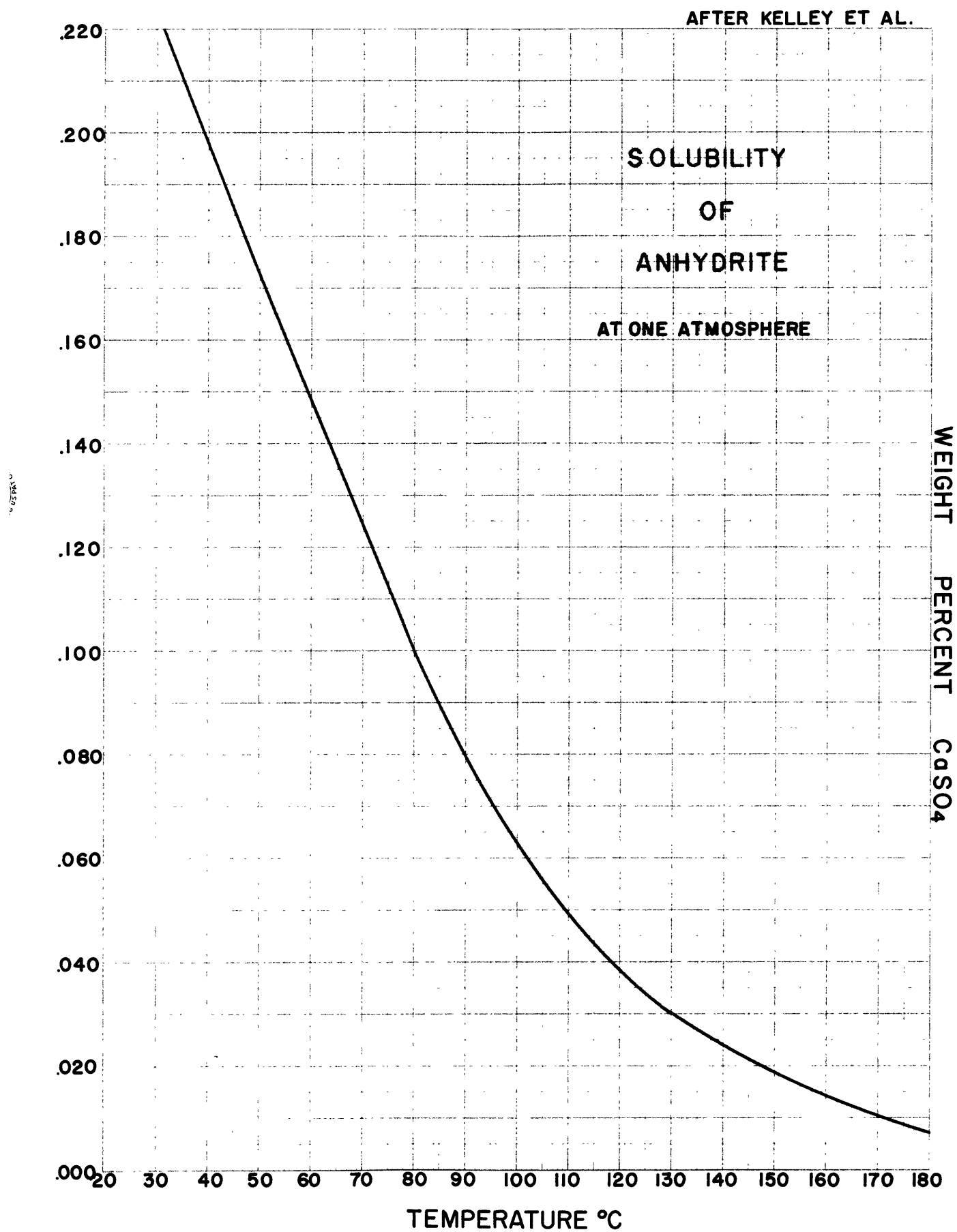


FIGURE 3.

the gypsum, this curve starts off at a maximum and steadily decreases with increasing temperature. Figure 4 is a solubility diagram combining the two curves. They intersect at about 40°C , which corresponds to the equilibrium temperature of gypsum and anhydrite in pure water at a pressure of one atmosphere. Above this temperature anhydrite is the stable phase, whereas at lower temperatures gypsum is the stable phase, since the less soluble substance is always the more stable one. Figure 4 also includes a curve³⁰ for the solubility of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} (\alpha)^*$ ---as before, the asterisk is the symbol Kelley uses to show that there is evidence indicating that the hemihydrate contains extra water (held in solid solution) when it itself is in contact with water. The curve intersects the solubility curve for gypsum at about 97°C , and above this temperature $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} (\alpha)^*$ can exist in contact with water under conditions of metastable equilibrium for "any reasonable period of time."³⁰ Table I gives data on the values of solubility for these three curves, along with the sources from which they were obtained.

Although parts of the solubility curves are given by Kelley and others, they have not been put together in the standard form of a phase diagram, indicating the regions in which the different compounds are stable or can co-exist. In the study of the geologic deposition and metamorphism of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and its dehydration compounds, only a small

AFTER KELLEY ET AL.

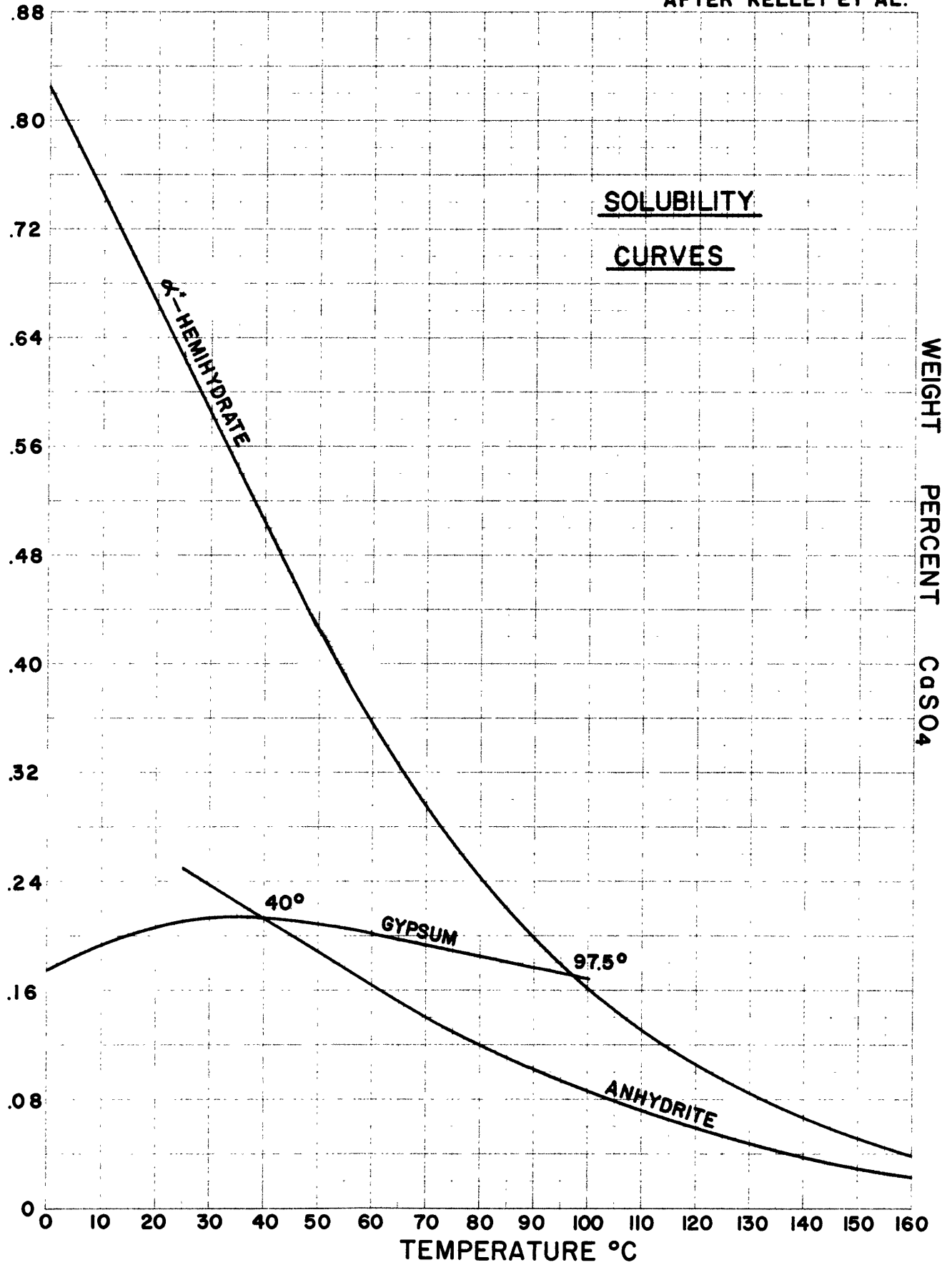


FIGURE 4.

TABLE I
Solubility of Anhydrite at 65°C²⁸

Initial Concentration	From Undersaturation, %	From Supersaturation, %
	0.00	2.229
25 days	0.136	0.173
4 months	0.135	0.152

Solubility of Anhydrite at 45°C²⁸

Time, Days	From Undersaturation, %	From Supersaturation, %
0	0.00	0.211
28	0.200	0.210
88	0.201	0.211

Solubility of Anhydrite at 35°C²⁸

Time, Days	From Undersaturation, %	From Supersaturation, %
0	0.00	0.250
28	0.242	0.245
80	0.242
Gypsum	0.212

Solubility of Anhydrite³⁰

Temperature, °C	Weight Percent CaSO ₄	Temperature, °C	Weight Percent CaSO ₄
40	0.221	120	0.038
60	0.149	140	0.024
80	0.100	160	0.014
100	0.063	180	0.007

Solubility of Gypsum²⁹

Temperature, °C	Weight Percent CaSO ₄	Temperature, °C	Weight Percent, CaSO ₄
0	0.176	35	0.2117
10	0.193	40	0.2115
20	0.206	60	0.201
25	0.209	80	0.185
30	0.211	100	0.169

portion of such a phase diagram would be of interest. This present study is an attempt to present the available information, and also to add to the known data some new determinations on the effects of pressure and temperature on the transition point of gypsum and anhydrite.

Hill²⁸ attempted to find the transition temperature of gypsum and anhydrite by studying the solubility of anhydrite at different temperatures, trying to approach the equilibrium point from two directions. Some of his results are given in Table I, and it is pointed out here that the time factor is important in all experimental work dealing with the solubility of calcium sulphate. For it can be seen from Hill's figures that even for periods as long as five months equilibrium may not be uniquely reached when attempts are made to approach it from both undersaturation and supersaturation at a pressure of one atmosphere, although the differences in solubilities generally get smaller and smaller as more time is allowed for the determinations.

To get more details on the deposition of calcium sulphate from evaporating sea water, Posnjak⁴⁵ formed a solution similar to present day sea water and investigated the solubilities of gypsum and anhydrite in such a solution at 30°C. He then formed a solution of twice this concentration and repeated the work, and so forth on up to a 5.5 "normal" solution. The actual concentrations of salts he used are given in Table II. His results are listed in Table

TABLE II

Composition of sea water used in solubility determinations⁴⁵

Compound	Sea Water Composition, Challenger Expedition, Parts Per Liter	"Normal" Solution Used, Parts per Liter
NaCl	27.213	27.2
MgCl ₂	3.807	3.8
MgSO ₄	1.658	1.7
CaSO ₄	1.260	...
K ₂ SO ₄	0.863	0.9
CaCO ₃	0.123	...
MgBr ₂	0.076	...

TABLE III

Solubilities of gypsum and anhydrite in sea salt solution⁴⁵

Concentration of sea salt solution	Gypsum Grams per 100 grams H ₂ O	Anhydrite Grams per 100 grams H ₂ O
0.0	0.209	0.250
0.5	0.366	0.414
1.0	0.418	0.468
2.0	0.449	0.488
3.0	0.432	0.470
3.6	0.412	0.436
5.0	0.339	0.336
5.5	0.308	0.288

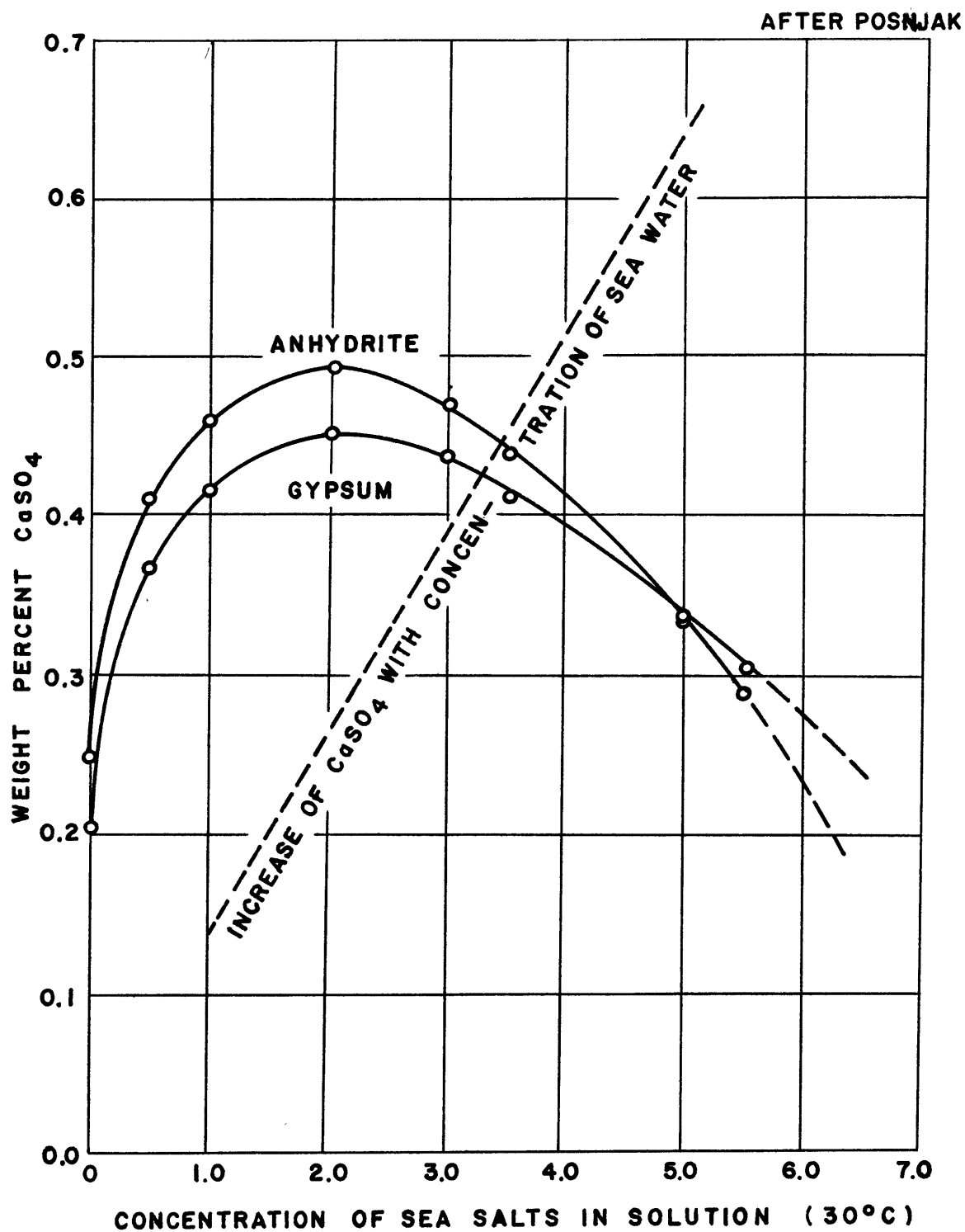


FIGURE 5.

III, and plotted in Figure 5 along with a line showing the normal increase of concentration of calcium sulphate in sea water as it evaporates. Both gypsum and anhydrite show retrograde solubility in this sea salt solution, but the solubility of anhydrite decreases at a more rapid rate after reaching its peak at twice the normal concentration, and intersects the gypsum curve at 4.8 times the normal salinity. The line indicating the increase of calcium sulphate concentration intersects the gypsum solubility curve at 3.35 times the normal concentration of sea water. Thus, at 30°C, and assuming this concentration of sea water, gypsum will be deposited as the stable phase when the sea water is concentrated 3.35 times, and anhydrite will become the stable phase at 4.8 times the normal concentration. It should be noted that at the latter point the solution will still be at less than one half the saturation point for sodium chloride. If complete evaporation takes place, less than half the calcium sulphate originally present would be precipitated as gypsum, the remaining portion being deposited as anhydrite.

PHASE DIAGRAM

The $\text{CaSO}_4\text{---H}_2\text{O}$ system, if in stable equilibrium, can possess a maximum of only two compounds, or solid phases, besides ice. These are the insoluble anhydrite and the dihydrate. The saturated solution in contact with them at the

transition point is called an inevaporable solution,¹⁴ because if heat is slowly applied, the temperature and composition of the solution will remain constant, the absorption of heat by the dissolving solids balancing the addition of heat into the solution. Furthermore, there will be no change in the quantity of the solution, since the amount that evaporates is balanced by the addition of water from the dissolving dihydrate. This, of course, will only hold true if both the dihydrate and anhydrite are present. There are three phases to this system; the anhydrite, the dihydrate, and the liquid in contact with them. The two components of the system are CaSO_4 and H_2O . The system is univariant according to the phase rule $F = C - P + 2$, where C is the number of components, P the number of phases, and F the number of degrees of freedom of the system. Thus, $F = 2 - 3 + 2 = 1$, that is, there is one degree of freedom, the variable being the pressure, temperature, or composition. If the pressure is held constant there are zero degrees of freedom, and the system is completely defined. For a pressure of one atmosphere, equilibrium can only exist between gypsum, anhydrite, and a saturated calcium sulphate solution at about 40°C . At higher pressures, according to thermodynamic calculations by MacDonald³⁷ and experimental determinations described later, the equilibrium temperature will increase linearly at the rate of about 85.4 bars per degree. Thus, at 46°C the equilibrium pressure is about 500 bars.

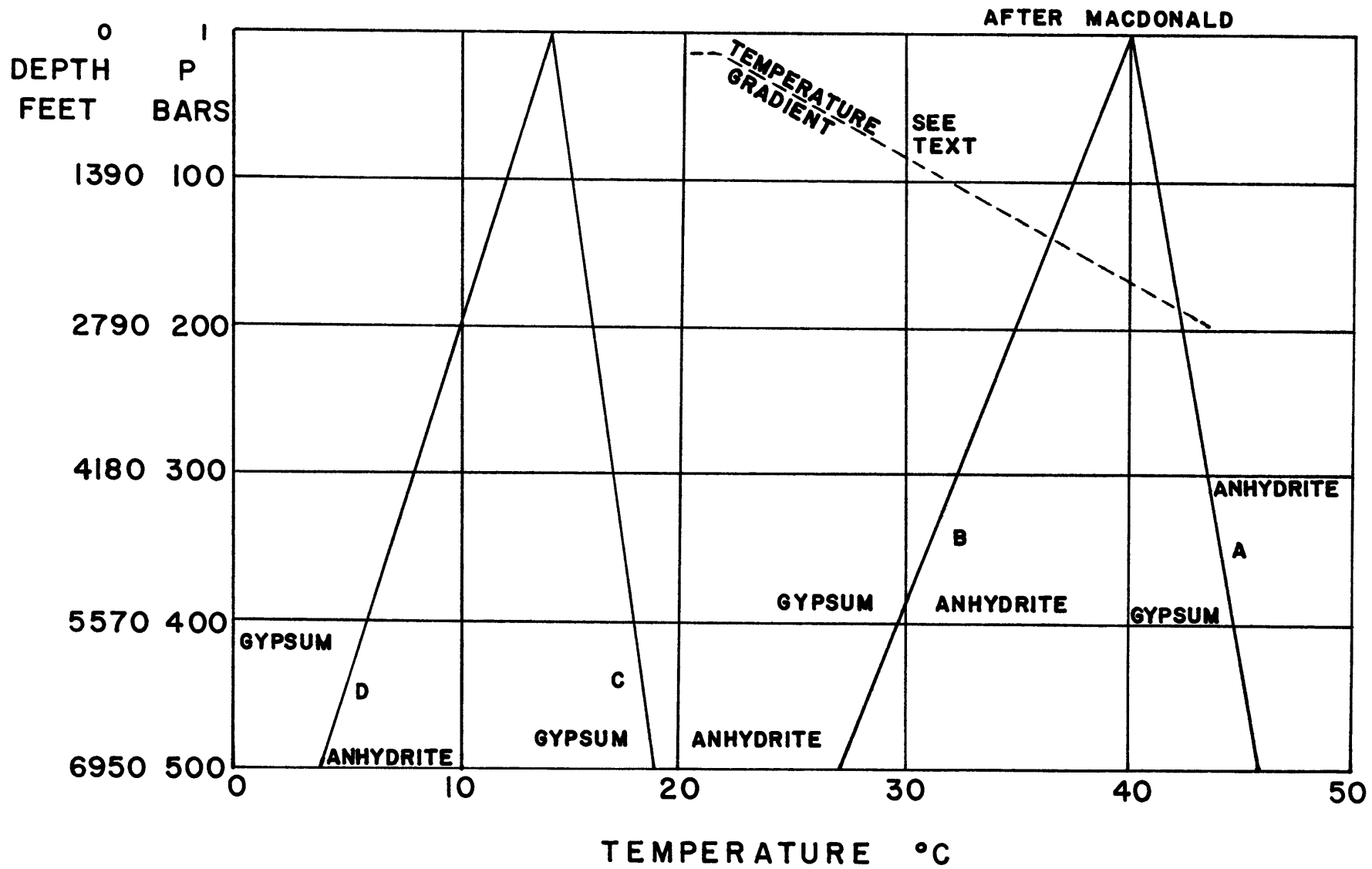


FIGURE 6.

However, MacDonald calculated this to be true only for the same hydrostatic pressure acting equally both on the surrounding solution and on the solid phases. If the pressures are unequal, that is, if there is a lithostatic pressure 2.4 times the hydrostatic pressure acting on the solid phases, his calculations then show the change in equilibrium temperature with pressure has a negative slope of 39.45 bars per degree. At 27°C the equilibrium pressure would be 500 bars. Both these curves are illustrated in Figure 6 and will be referred to later.

Where only one of the solid phases, either the anhydrite, the gypsum, or the ice, is in equilibrium with the liquid, the system is bivariant. (There are two components and two phases; hence, $F = 2 - 2 + 2 = 2$, that is, there are two degrees of freedom.) If the pressure is held constant then the temperature is the only variable and completely determines the composition of the liquid.

At the cryohydric point (commonly known as the eutectic point but called "cryohydric" in aqueous solutions when one of the solids is ice), where both the ice and gypsum are in equilibrium with the liquid, there are again three phases and therefore, the variance of the system is one. Hence, at constant pressure the cryohydric point is completely determined. For one atmosphere, the author found this to be $-0.7^{\circ} + 0.1^{\circ}\text{C}$ (see Chapter II, CRYOHYDRIC POINT).

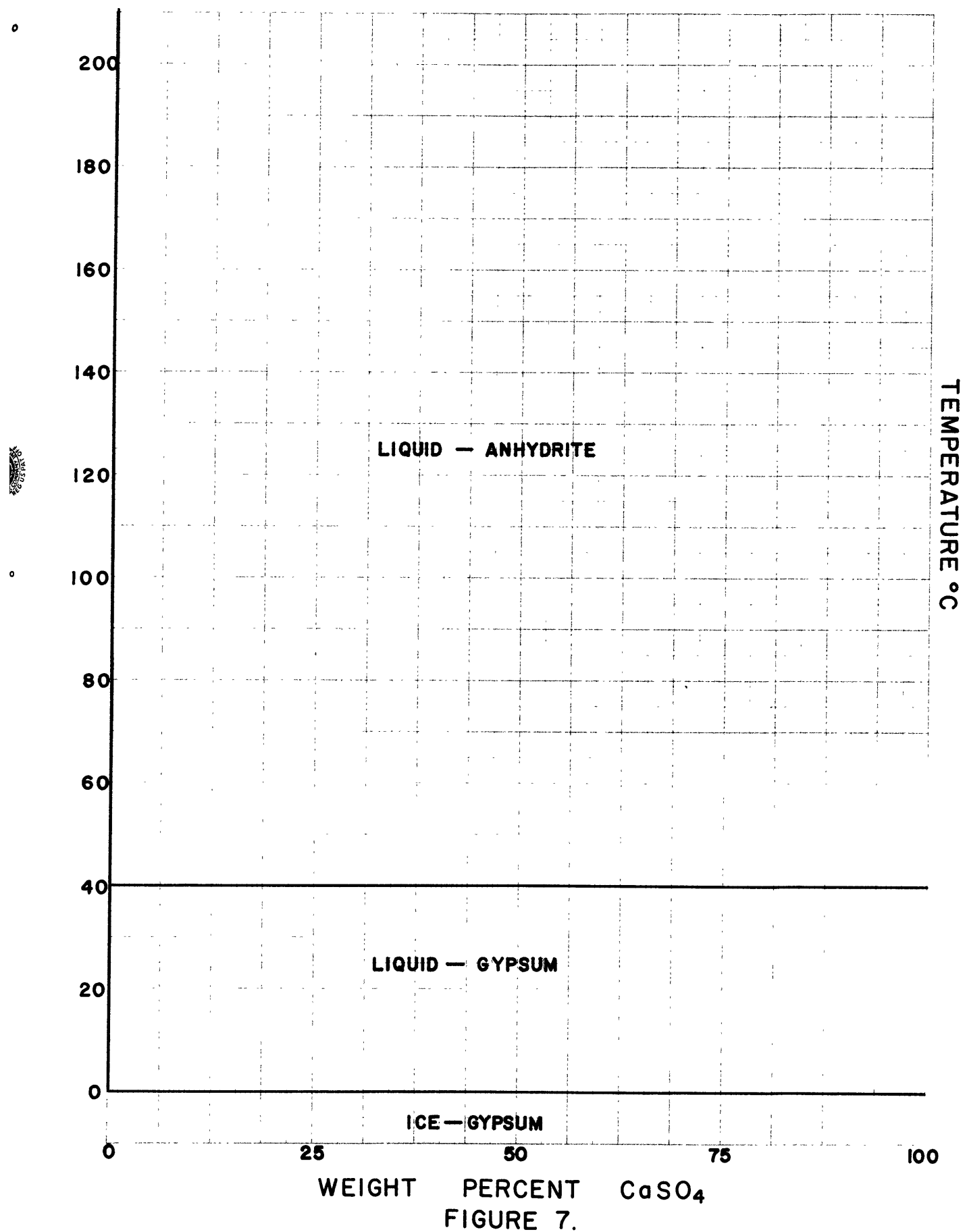


Figure 7 is a phase diagram of the stable calcium sulphate compounds in an aqueous solution. It was prepared by combining the previously discussed solubility curves and the cryohydric point. Inasmuch as the solubility of both gypsum and anhydrite are so extremely low, the curves separating the liquid and solid phases are touching the pure water axis. Therefore, Figure 8 was drawn to illustrate those details which have more significance to geologists. By this is meant the fact that although gypsum and anhydrite are chemically relatively insoluble, they are considered one of the more soluble minerals and rock deposits in the geologic environment where time can easily extend into the thousands and millions of years and where a fresh supply of unsaturated water can slowly dissolve and then perhaps redeposit the calcium sulphate as gypsum or anhydrite as temperature, pressure, and salt saturation conditions slowly change. The phase diagram illustrates some of the important features of calcium sulphate deposition. The best way to show the reactions and change of phases is to choose a specific concentration on the diagram and follow an isopleth (line of constant concentration) as the temperature is varied.

A first example is an aqueous solution containing 0.100% calcium sulphate by weight, represented by point A. If heat is added, the temperature is raised until it reaches about 90°C , at which point the liquid and anhydrite will be

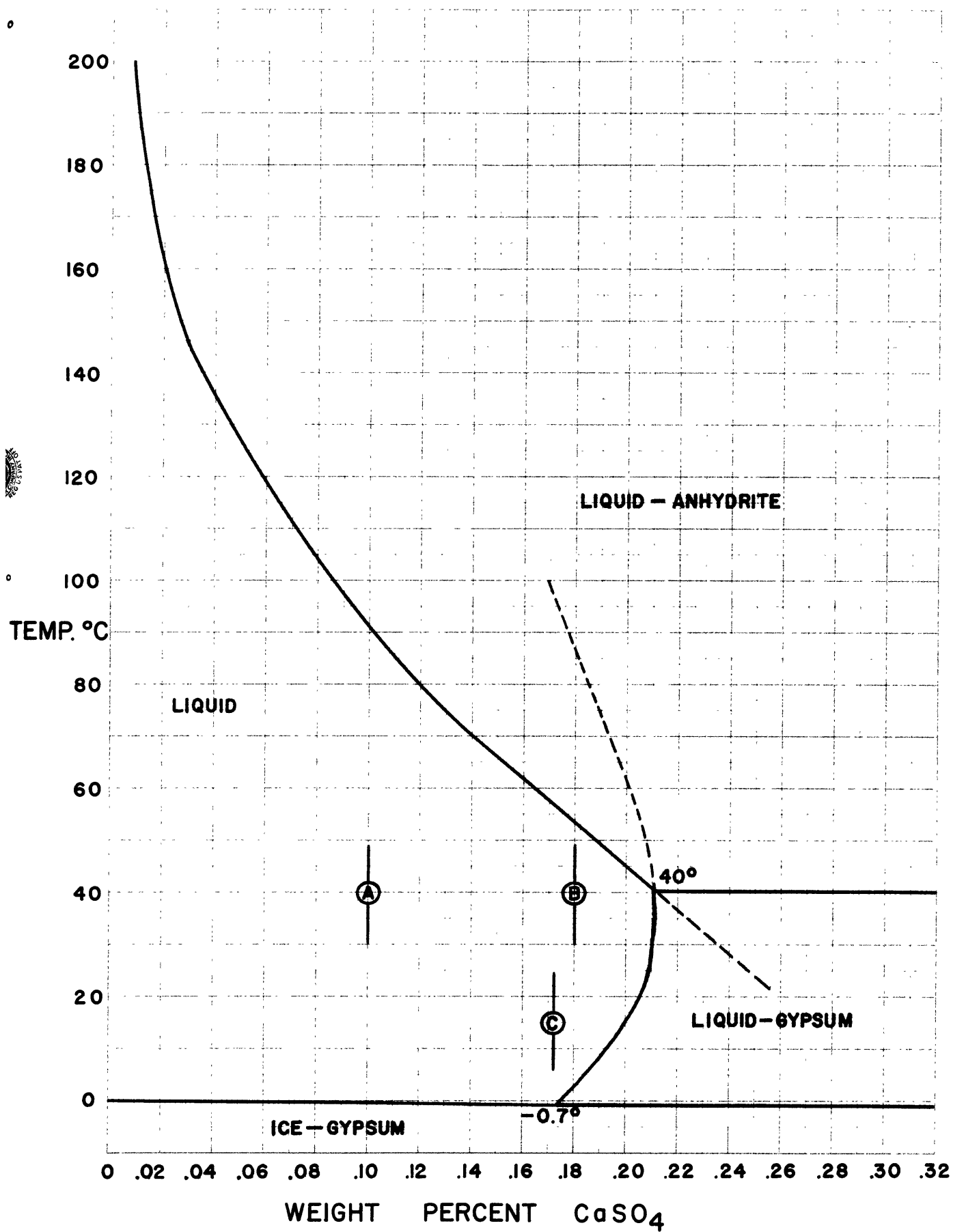


FIGURE 8.

in equilibrium. As more heat is added, anhydrite begins to crystallize out and is slowly precipitated at the expense of the solution which becomes less concentrated. This continues until a temperature of 200°C is reached, where the solution contains only 0.008% calcium sulphate. There is no further information beyond this point and it can only be speculated as to what happens as higher points on the temperature axis are reached. Assuming that no new forms of calcium sulphate appear, it is likely that the equilibrium line separating the liquid and the anhydrite phases will continue slowly approaching the zero isopleth until the critical point for the solution is reached, probably very near the critical point of water since there is so little solute dissolved in the liquid phases at or near that temperature.

If, instead of raising the temperature at point A, heat is taken out of the solution, the temperature will be progressively lowered along the 0.100% isopleth until -0.4°C is reached, when ice will begin to form. As more heat is removed, the concentration of the liquid will increase and more ice will form, following the liquid-ice equilibrium line down to the cryohydric point. Here gypsum will start crystallizing out and will be in equilibrium with both the ice and the liquid. At this point, since there are three phases and two components, the system will be univariant ($F = 2 - 3 + 2 = 1$). If the pressure is held constant at

one atmosphere, the cryohydric temperature is about -0.7°C , as found from direct experiment which will be described later. After the liquid has completely solidified into a mixture of ice and gypsum, the temperature will continue dropping. It is to be noted here that the two solid phases form a true mixture and not a solid solution.

A second example is taken to the right of the cryohydric point and in the liquid region, marked as B on the diagram. The concentration is 0.180% calcium sulphate by weight. If the temperature of the solution is raised, it will follow an isopleth up to about 53°C where anhydrite will begin to crystallize out of the solution. The concentration will then decrease as the liquid-anhydrite equilibrium curve is followed up to the left and will then follow exactly the same path as that described for point A. If the temperature at point B is decreased, however, gypsum will be the first solid phase to form, at a temperature of about 2°C . The gypsum-liquid equilibrium curve will then be followed down to the left till the cryohydric point is reached, and the same reaction will occur as described before.

A third example is a solution of exactly the same concentration as that of the cryohydric point, marked as point C. There will be about 0.172% calcium sulphate by weight in such a solution. As the temperature is lowered to the cryohydric point, both gypsum and ice will crystallize out at the same time until there is no liquid left. As

before, this will be a mixture of the two and not a solid solution.

Because of its retrograde solubility, calcium sulphate will be deposited out of solution when near saturation whether the temperature is raised or lowered, with the higher temperature form being anhydrite and the lower temperature form being gypsum. This is an interesting point, for it can show the mechanism whereby a gypsum deposit hypothetically can be wholly converted to anhydrite by only a small amount of water, with or without a temperature change, so long as the final temperature is above the transition point. As soon as the water is in contact with the gypsum it passes some of the solid into solution until the saturation point is reached. If the original temperature is raised, more solute goes into the solution, following the gypsum-liquid equilibrium curve till about 40°C . Above this point, anhydrite is precipitated out of solution, since its solubility is less than that of gypsum. However, the metastable existence of gypsum above 40°C , as shown by the dotted portion of the curve, still indicates the relation between it and the liquid, and the process of dissolving will still occur as long as the liquid contains less calcium sulphate than indicated on this part of the solubility curve. The calcium sulphate thus passes from the solid dihydrate into solution, and then back into a solid phase again as the more stable anhydrite, till only the anhydrite is left. Further-

more, since there is 20.93% of water by weight in gypsum, this amount of liquid will be added to the solution and be available as solvent. If the original temperature is above the 40°C transition point, the same type of conversion takes place, that is, equilibrium between gypsum and the solution is trying to take place while at the same time equilibrium between the solution and the less soluble anhydrite is also occurring. Since the process of gypsum solution and deposition is not reversible above the transition point, anhydrite will crystallize out at the expense of the gypsum.

Similarly, an anhydrite deposit in contact with water below the transition point will be completely or partially converted to gypsum, the amount of conversion depending upon the quantity of water available for hydration. The time factor for these changes is not as important geologically as it is in the laboratory, where there is some difficulty in causing the conversions.

TRANSITION POINTS

Attempts have been made previously to cause these reactions in the laboratory, with only partial success. Goodman¹⁸ performed a group of four experiments in a study of gypsum and anhydrite under simulated conditions of deposition. The first experiment was an attempt to determine the stability range of these compounds in different concen-

trations of sea water under temperatures ranging from 19°C to 73°C and at a pressure of one atmosphere. By placing gypsum or anhydrite in these solutions in sealed test tubes, and then waiting from 64 days to a year before re-examining the solids, he found that positive conversions occurred only at the higher and lower temperature ranges. At the intermediate temperature of 50°C he found the transitions "extremely slow." It is to be noted that conversions to the hemihydrate occurred, and that Goodman seriously considers the possibility of this reaction also taking place in the geologic deposition of gypsum or anhydrite, with a later conversion to a more stable phase. He admits, however, that there is no evidence in nature for this hypothesis, such as the existence of pseudomorphs of anhydrite or gypsum after hemihydrate.

A second experiment tried to show the effect of different concentrations of magnesium, calcium, potassium, and the sulphate and carbonate radicals on the transition point. At 17°C gypsum was always the stable phase, no matter what the concentration. At 73°C it was found that adding magnesium gave inconclusive results, adding calcium "favoured the formation of anhydrite," adding potassium probably raised the transition point close to this temperature, and adding sulphate and carbonate "favoured the formation of the hemihydrate."

In another experiment Goodman found that if anhydrite was left in varying amounts of pure water at about 19°C for 520 days, then the greater the amount of water the smaller the amount of hydration to gypsum would occur. If there was just enough water for complete hydration, 19% of the anhydrite was altered; if five times this amount of water, 5% was altered; if nine times this amount, only 2% was altered. This is explained by the low solubility of anhydrite and long time required for a solution to become saturated with calcium sulphate. Goodman states that "the mechanism by which anhydrite alters to gypsum, as indicated by this and other experiments, is not a simple absorption of the amount of water required but is a process of solution of the anhydrite and reprecipitation of gypsum." Saturated calcium sulphate solutions, microcrystallinity, and porous material, therefore, favors alteration since they provide the favorable reprecipitation conditions.

HYDRATION MECHANISM

The hydration just mentioned was previously stated by Posnjak¹⁴ in a paper in which he criticized some of the work done by van't Hoff and his associates about fifty years ago on some of the problems encountered in the study of gypsum and its dehydration products. Apparently, van't Hoff came to the conclusion that gypsum could recrystallize directly into insoluble anhydrite, without going through the inter-

mediate hemihydrate and soluble anhydrite stages. This is erroneous, and in general "all reliable experimental evidence uniformly shows that, for a series of hydrates, the dissociation always results in the formation of the compound that is next in composition."⁴⁴ For the dehydration and complete breakdown of gypsum, this statement is well illustrated in the thermograms of gypsum (see Figure 17) which always show the endothermic peaks of the formation of the hemihydrate and the soluble anhydrite, and the exothermic peak of the transformation to the insoluble or natural anhydrite. Posnjak found that if gypsum was placed in water and heated to $97.5 \pm 1^{\circ}\text{C}$, it would form hemihydrate, a confirmation of the same result found by Partridge and White.⁴³ An interesting experiment he carried out was to place pure gypsum in water at one atmosphere pressure and 75°C for a period of two years. At the end of that time, the gypsum was unchanged. However, upon duplicating the experiment, except for the placing of a small amount of anhydrite in with the gypsum, the whole thing completely changed to anhydrite. Thus, he showed the metastability of gypsum at that temperature was sufficient to maintain it unchanged, unless it was seeded with the stable phase. This is an important point in conducting experiments on the stability of gypsum, for even though well above the transition point anhydrite may not form unless there is actually a small amount of it present to initially start the reprecipitation.

Posnjak also determined the transition point for gypsum and anhydrite on the basis of solubility measurements and found it to be 42°C , the same temperature found by Hill²⁸ in his study of the transition. Hill also determined the solubilities of gypsum and anhydrite at 35°C in the presence of different concentrations of potassium sulphate solution. Posnjak then extrapolated these curves to find the point of concentration at which gypsum and anhydrite are in equilibrium with each other. In a later paper⁴⁵ however, Posnjak said this extrapolation was erroneous because his own measurements of the solubility of gypsum and anhydrite in a potassium sulphate solution gave different results. The effect of potassium sulphate, as found by Hill, is to lower the solubilities of both gypsum and anhydrite, but what is more important in a discussion of the transition point, is the fact that he found that the solubility of anhydrite is lowered at a greater rate than the solubility of gypsum. Because of the common $\text{SO}_4^{=}$ ion, the solubility is lowered in this case, but with other salts, such as sodium chloride, the solubilities are raised. The determining factor in finding a change in the transition point is whether the added salt solution affects the solubilities such that the gypsum and anhydrite curves intersect. As Posnjak points out, it may take only a small amount of salt to lower the transition point considerably.

EFFECT OF PRESSURE

Except for two unsuccessful experiments by Farnsworth,¹³ no experimental information is available on the effects of pressure on the temperature transition points of gypsum and anhydrite. Miss Farnsworth used the sealed test tube method similar to that of Goodman,¹⁸ with either gypsum or anhydrite surrounded by pure water. When the tubes were heated, the vapor pressure of the water rose to a higher value, depending entirely on the temperature. The effect of the dissolved calcium sulphate on the vapor pressure was negligible, due to its very low solubility. The temperatures varied from 100°C to 210°C, in steps of 10°, and 48 hours was the time involved for each test. The results were disheartening, for the main purpose of the experiments was to try and find a means of hydrating anhydrite. The anhydrite was found to be unchanged at all the temperatures tried. The gypsum was unchanged at 100°C, half converted to hemihydrate at 110°C, and completely converted to the hemihydrate from 120°C to 160°C, at which point it changed into anhydrite. From 160°C to 210°C, anhydrite was always formed. At 160°C the pressure in the tubes was about 6 atmospheres, and at 210°C it was about 19 atmospheres. One important criticism of her work is that she did not allow enough time for the conversions to take place, considering that she could not detect very small changes that would indicate the beginning of a reaction which, if given enough

time, would go to completion. This is corroborated by Posnjak's⁴⁴ and Partridge and White's⁴³ experimental determinations of the gypsum-hemihydrate transition in water at $97.5 \pm 1^\circ\text{C}$, whereas Miss Farnsworth didn't notice the transition till well over 100°C . Her conclusion was that "these tests indicate that anhydrite can not be rehydrated under conditions of high temperature and pressure." The experiments conducted by the author indicate that this statement is a bit premature, for although temperatures in this relatively high range were not used in the determinations, positive evidence for conversion of anhydrite to gypsum under high pressures was found.

MacDonald³⁷ has calculated the transition points from one atmosphere up to about 500 atmospheres (see Figure 6) from thermodynamic data supplied by Kelley³⁰ and others. These calculations are for equal pressures on both the solid and liquid phases, for lithostatic pressures 2.4 times greater than the hydrostatic head, and for the effect of dissolved sodium chloride in the saturated aqueous solution. However, in applying his results to conditions within the earth's crust, he has not taken into consideration the characteristics of gypsum and anhydrite deformation. Some of the geologic environmental conditions in gypsum and anhydrite deposits can be approximated or assumed, such as temperature, pressure, and salinity, and from these calculations can be made that will essentially be correct. How-

ever, unless the approximations and assumptions fit the geologic conditions, the true behavior of these substances will not be known. Thus, while it may be true that at a pressure of 500 bars in pure water the gypsum-anhydrite transition temperature is lowered from 46°C to 27°C when the lithostatic pressure is increased to 2.4 times the hydrostatic pressure,* it may be impossible to produce this

* The method by which this could be experimentally determined, without having any differential stresses applied to the gypsum or anhydrite that might cause flowage, would be to place the solid material in a bomb containing gaseous nitrogen under pressure as well as a certain amount of water vapor. The nitrogen would exert a "lithostatic" pressure on the solid, while the partial pressure of the water vapor would exert a similar, but lower, hydrostatic pressure.³⁸

difference in pressure under geologic conditions where deformation effects such as plastic flow, mechanical twinning, and rupture are taking place within the solid.

Compared to most other consolidated rocks, gypsum and anhydrite are relatively incompetent. Billings² summarizes the properties of alabaster by giving the dry strength as 480 kg/cm^2 , and the ultimate strength as 520 kg/cm^2 .

NOTE: One atmosphere is roughly equal to one kilogram per square centimeter. More precisely, one atmosphere equals 1.0332 kg/cm^2 . The difference is a little over three per-

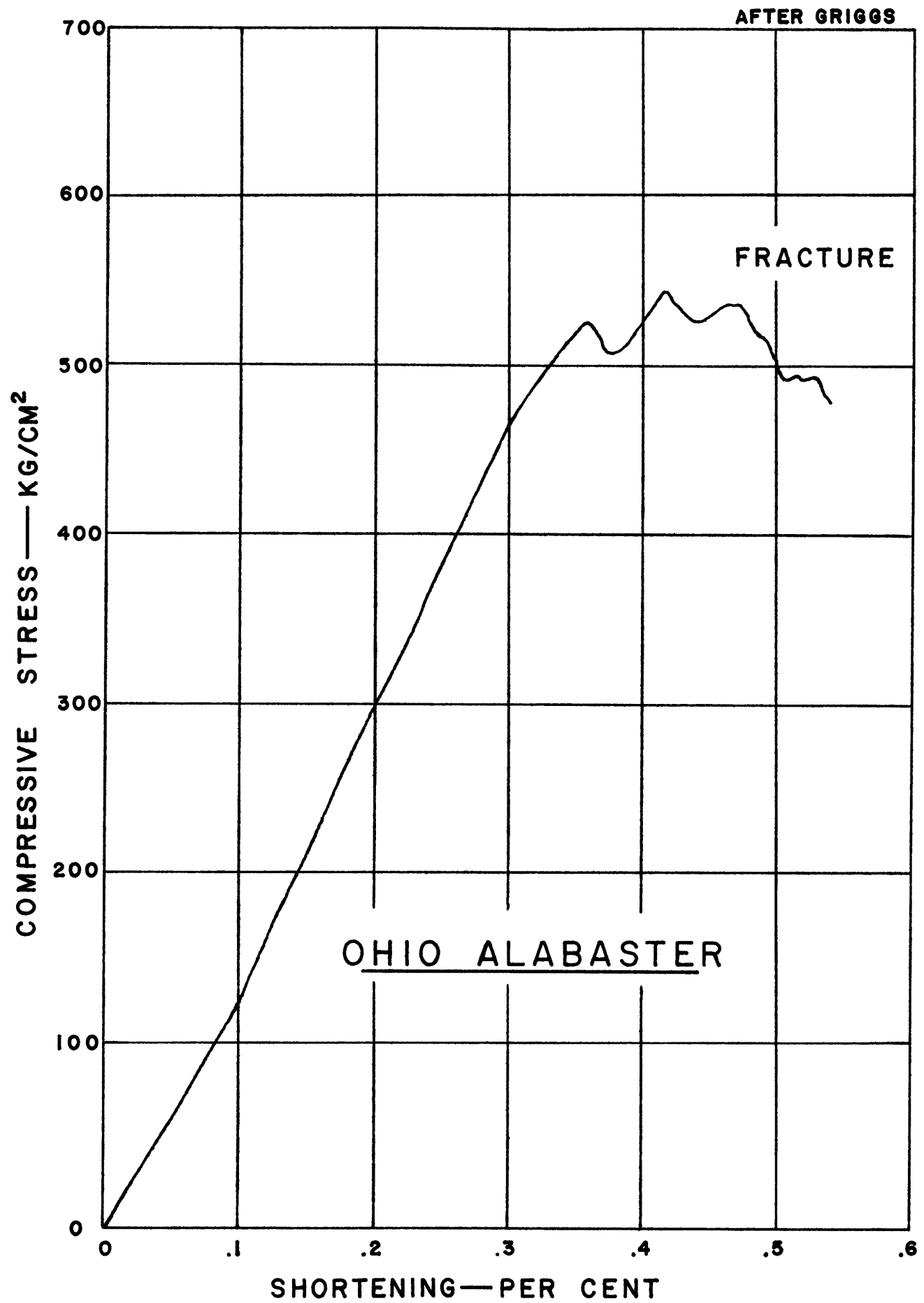


FIGURE 9.

cent, or about 17 atmospheres at 500 atmospheres.

However, when the material is free to react with water its strength drops down to about 92 kg/cm^2 . Griggs²⁴ has done experimental work and studied the flow of alabaster under conditions favoring recrystallization by applying stresses to the solid material when it was surrounded by its own aqueous solution. Figure 9 is a typical stress-strain diagram of the dry material, showing primarily elastic deformation, with some plastic flow taking place before rupture. This is a short time test. Under similar dry conditions and in a forty day period at a constant stress of 420 kg/cm^2 , the alabaster also deformed elastically, with the rate of deformation falling off with time, as shown by the straight line on the semi-log plot of Figure 10. However, when the specimen was surrounded by its own aqueous solution, the results were quite different. At 205 kg/cm^2 the deformation is greatly increased, and less so at 103 kg/cm^2 , as can be seen by the comparative curves in Figures 11 and 12 respectively. Figure 15 is a log-log plot of Figure 12. In a hydrochloric acid solution, the deformation is even greater, indicating that a solution process is likely the cause of the acceleration of deformation. However, when a common calcium ion was added to a pure water solution surrounding the alabaster and the experiment repeated, it was found that although the solubility of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ had been decreased by about 45%, the deformation was greater than

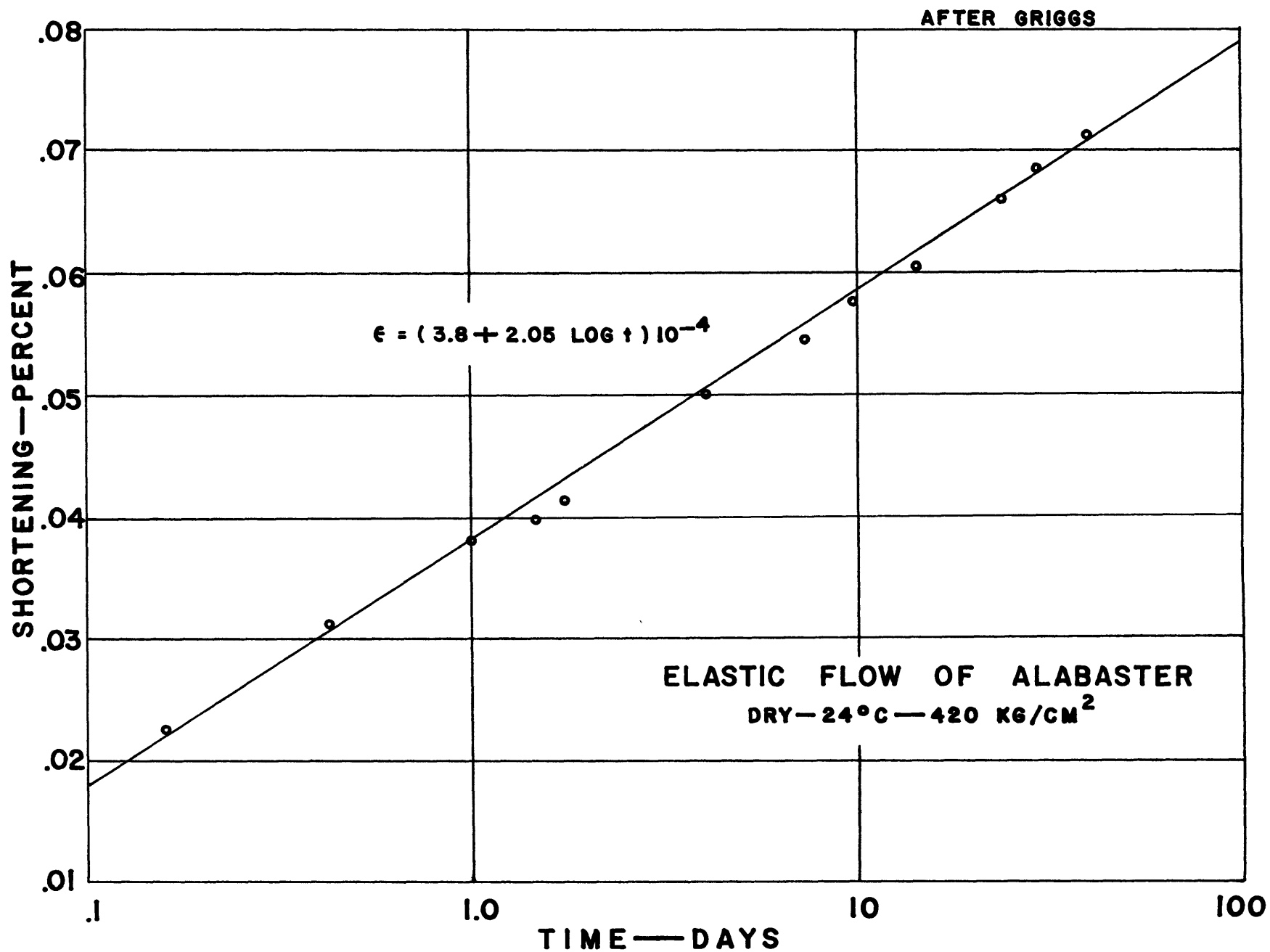


FIGURE 10.

that in pure water. Griggs inferred from this that the rate of flow was not a direct function of solubility. To determine the effect of time in the penetration of water into the interstices of the alabaster, a similar group of experiments were run after the samples were allowed to soak in pure water for a period of 68 days. The curves that were thus produced were essentially the same. In Figure 11 note that the rate of shortening decreases at the beginning of the test, then remains constant for a time, and then increases. Figure 13 shows a series of such curves for samples deformed under different pressures in pure water. Although not shown on the diagram, all the tests but the one at about 100 kg/cm^2 ended in rupturing of the specimen, after exhibiting the typical flat portion of the curve between the initial rise and the final increase of rate of deformation. If the flat or "steady-state" portion of the curve is considered an "equilibrium state of recrystallization flow," then we may take this as a fundamental constant of creep." These rates or velocities of flow can be plotted as shown on Figure 14, and the curve can be approximated by:

$$v = a \sinh b (\sigma - S) \quad (2)$$

where v equals the steady-state velocity, σ equals the compressive stress, and a , b , and S are empirical constants, 31, 0.0222, and 92 respectively for the latter three. Thus, it can be seen that at 92 kg/cm^2 the rate of flow will become zero, and Griggs calls this the "fundamental strength"

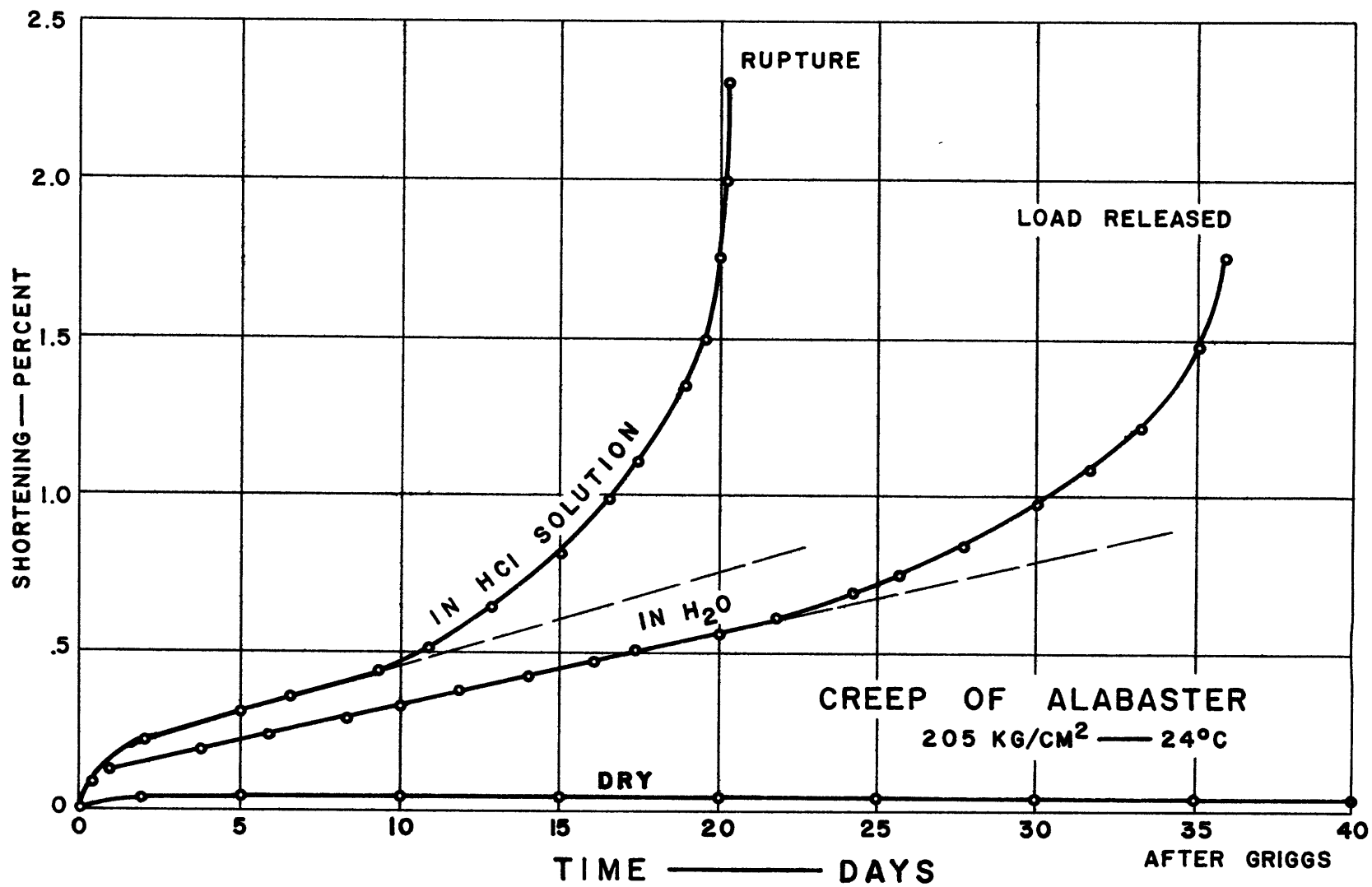


FIGURE II.

of the alabaster, under the conditions specified. One of these conditions is that there is a hydrostatic pressure of only one atmosphere on the alabaster, and therefore this figure is most likely not correct for greater hydrostatic pressures. Figure 14 also shows part of a curve for a hydrostatic pressure of 1000 atmospheres and it can be seen that its slope is different than that of the first curve. However, this difference is not considerable, although if an extrapolation can be made at all it would probably raise the "fundamental strength" of 92 kg/cm^2 somewhat. Inasmuch as no other data is available, the figure of 92 kg/cm^2 will be used in this paper as the lithostatic pressure that will cause flowage of gypsum, keeping the above interpretation in mind, however.

Goranson accounts for the initial high rate of flow (see Figure 13) by the application of the stress to the irregularities in the structure of the polycrystalline material.¹⁹ As these are removed by solution the stress undergoes redistribution and the pore spaces are filled. The stress then becomes evenly distributed and the deformation goes on at a steady rate, as described by the above equations. Finally, the material becomes stabilized and tends to behave as a single crystal, even though the individual crystal structures composing the mass may have random orientations. At this point, says Goranson, the rate of deformation will increase as gliding takes place along 45°

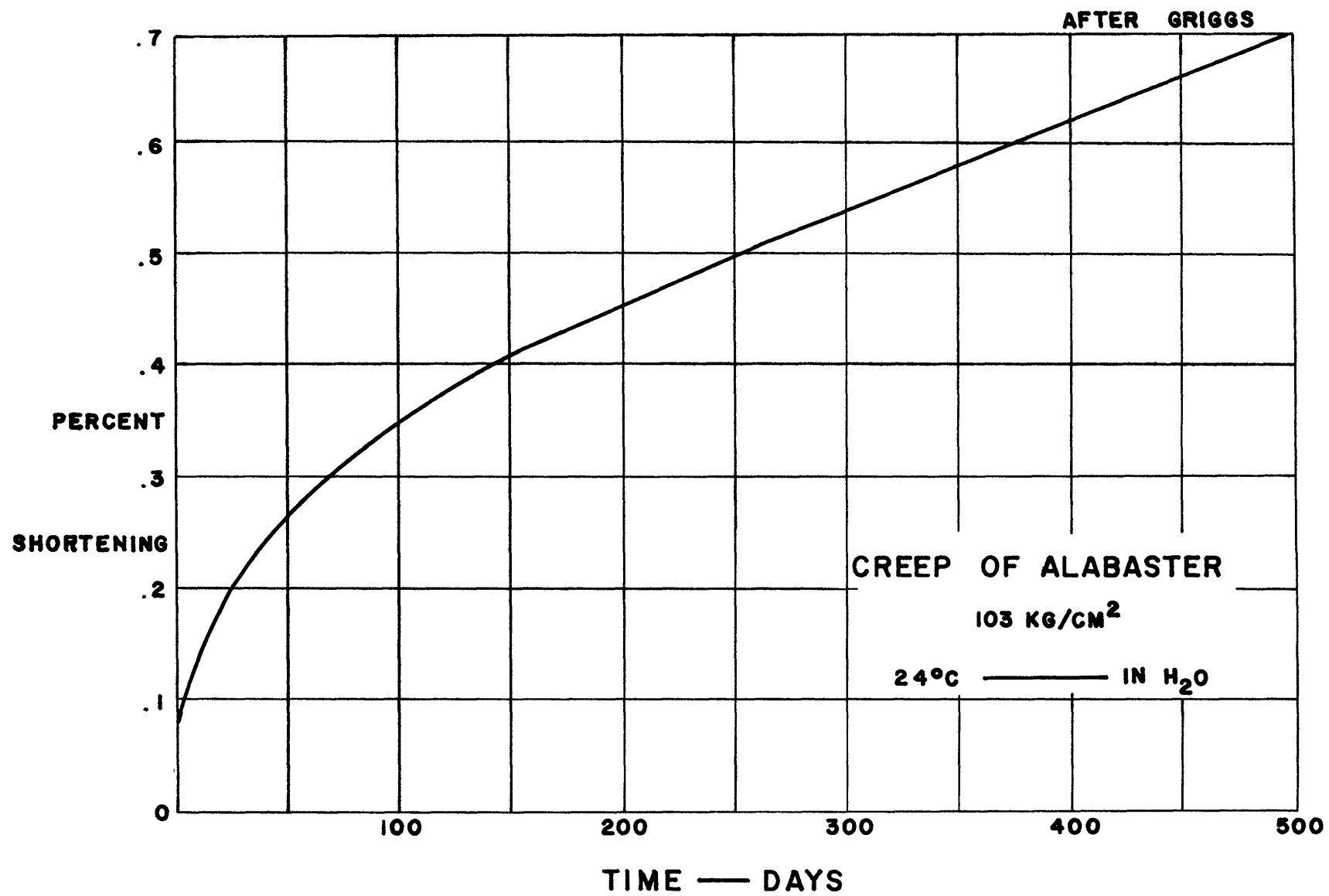


FIGURE 12.

planes until rupture occurs. This is for material surrounded by an aqueous solution not under any hydrostatic pressure. If a confining pressure is applied to the liquid, then the solubility relations are changed, as well as the concentration head between the stressed and unstressed faces and the mobility of the solute, the latter factor being the most important of the three. Up to 1000 atmospheres and more, the solubility of gypsum increases with increasing pressure, and this is also true of its mobility. Goranson computed the rate of flow of compressively stressed alabaster to be increased 1.5 times when it is surrounded by water under 1000 atmospheres pressure. Griggs' preliminary experiments determined this to be 1.6 times.

In Figure 13 Griggs points out an interesting feature of delayed fracture of alabaster. Between 0.45 and 0.55 percent deformation the rate of flow starts to increase and finally results in rupture of the specimen. He calls this inflection point the occurrence of "incipient fracture."

The existence of a threshold strength at 92 kg/cm^2 as indicated by Griggs is important in this study in that it can be applied to MacDonald's two calculated curves for the transition points of gypsum and anhydrite at different temperatures and pressures. The transition curve (see Figure 6) for a lithostatic pressure equal to 2.4 times the hydrostatic pressure will have to be altered when applied to geologic conditions, for at some depth the lithostatic

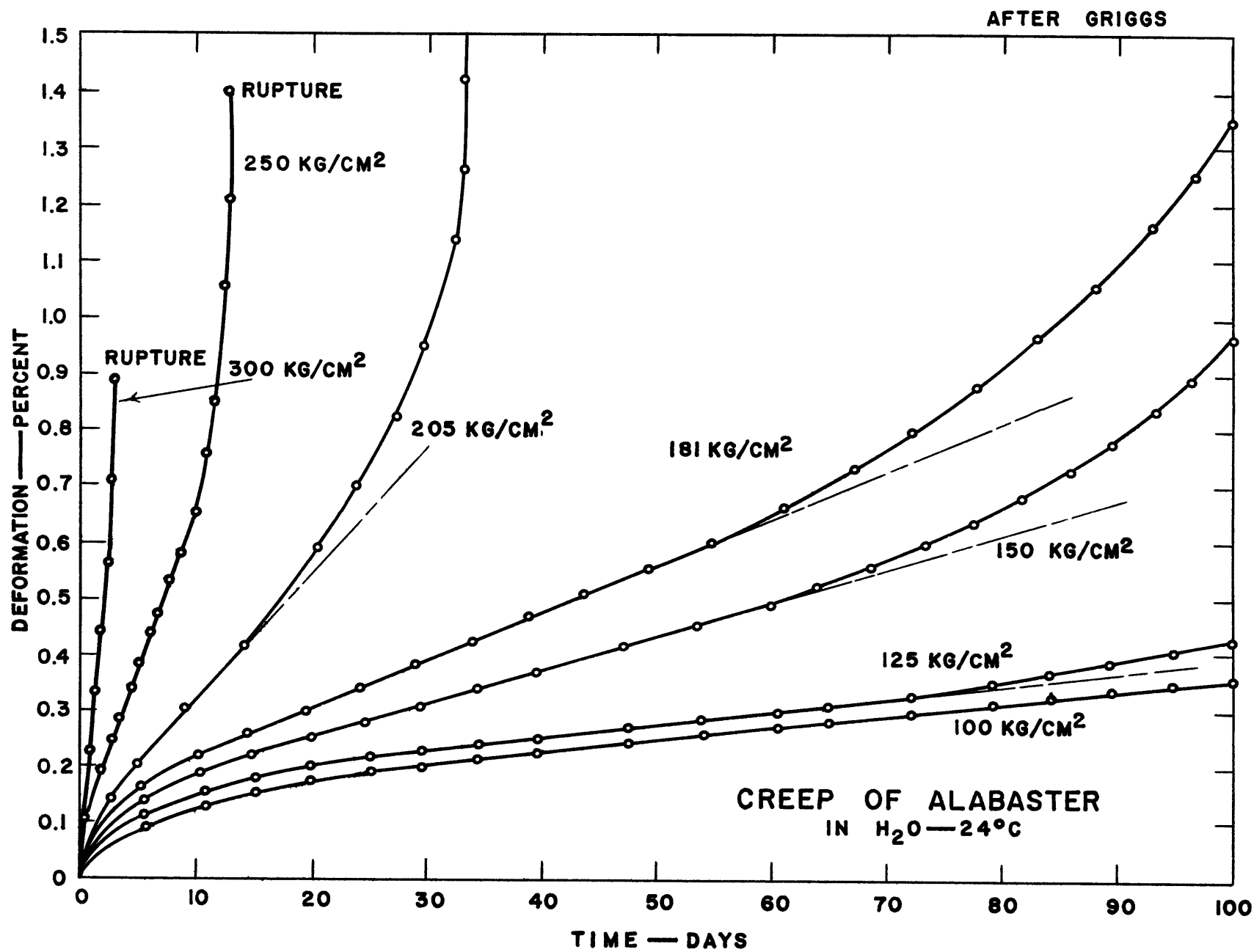


FIGURE 13.

pressure will be great enough to cause the gypsum to flow, tending to seal off and fill the pore spaces that contain the saturated aqueous solution. This will gradually increase the hydrostatic pressure on the liquid and tend to equalize it with the lithostatic pressure, which would then have the effect of just one hydrostatic pressure on both the solid and the liquid phases. Curve A of Figure 6 would then describe these conditions, once flowage of the solid phase and sealing off of the liquid phase has occurred.

If the pressure is great enough to cause flowage of the solid phase, it would be expected that the porosity of this material would then be low. Goodman¹⁸ has measured some samples of Nova Scotia gypsum and found their porosity to vary from 1.41% to 1.66%, which is rather low for a rock, although a chemically deposited sediment might be expected to have a low porosity anyway once it has become consolidated. He also measured the porosity of some Nova Scotia anhydrite, and found it so low as to be negligible.

DEPOSITION FROM SEA WATER

If a body of sea water is allowed to evaporate in an isolated basin, a series of chemical sediments will gradually be precipitated, often in a complex manner, as a definite succession of salts. An average of 77 analyses²¹ of sea water shows it to contain the following percentages of ions, based on a total salinity of 3.5%:

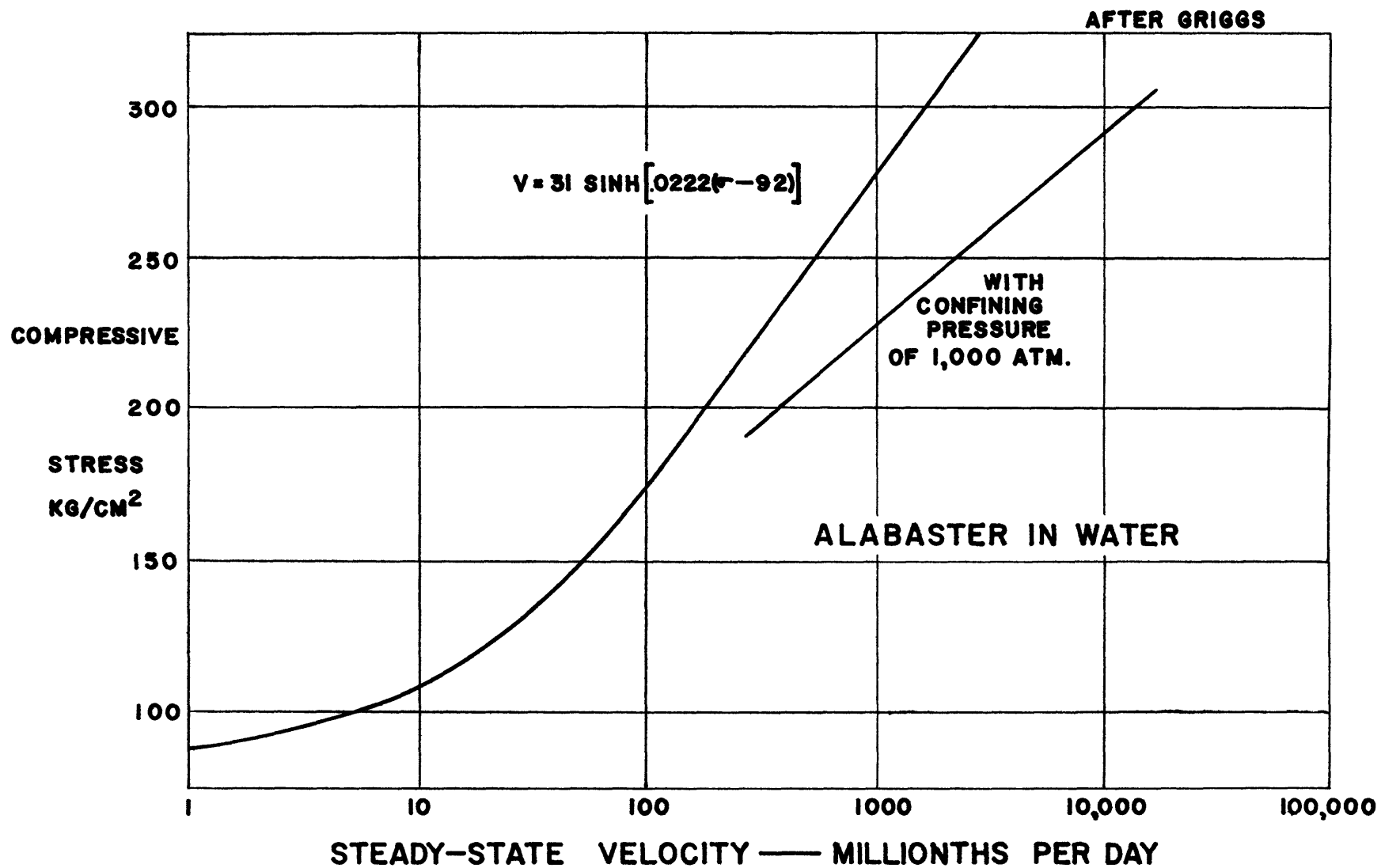


FIGURE 14.

TABLE IV

Cl.....	55.292
Br.....	0.188
SO ₄	7.692
CO ₃	0.207
Na.....	30.593
K.....	1.106
Ca.....	1.197
Mg.....	3.725
	<u>100.000</u>

If calculated as salts, the analyses would be as follows:

TABLE V

ANALYSIS OF SALINE MATTER OF OCEAN WATER, CALCULATED AS SALTS²¹

<u>Salt</u>	<u>Molecular Weight</u>	<u>Specific Gravity</u>	<u>Per cent Total Solids</u>	<u>Permillage or Grams per Liter</u>
NaCl	58.5	2.17	77.758	27.213
MgCl ₂	95.3	2.18	10.878	3.807
MgSO ₄	120.4	2.65	4.737	1.658
CaSO ₄	136.1	2.97	3.600	1.260
K ₂ SO ₄	174.1	2.465	0.863
CaCO ₃ *	100.0	2.72	0.345	0.123
MgBr ₂	184.3	0.217	0.076
TOTAL			<u>100.000</u>	<u>35.000</u>

*Including all traces of other salts.

As evaporation proceeds, the less soluble salts will proceed to evaporate, while the more soluble ones will become more concentrated. Lindgren³⁶ reports "experiments by J. Usiglio on sea water showed that the carbonates of calcium and magnesium, with a little ferric oxide, were precipitated when one liter of the water was reduced from one-half to one-fifth. Gypsum was precipitated when the volume was one-fifth to one-seventh, but continued in

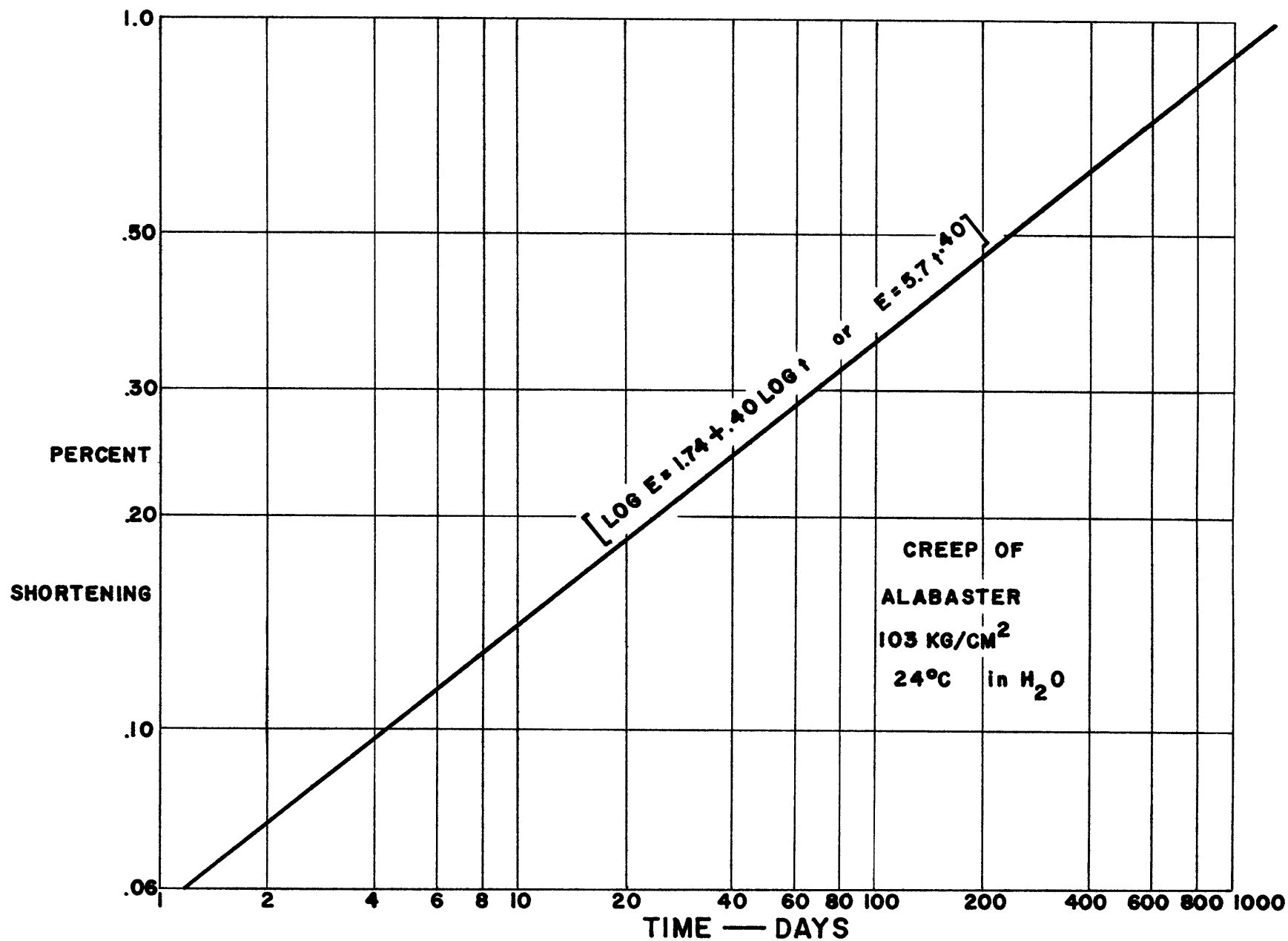


FIGURE 15.

lessening amounts until only 30 cubic centimeters of the original liter remained. Sodium chloride, the main constituent, was precipitated abundantly upon reduction of volume to 100 cubic centimeters, but continued until the volume of water was only 16 cubic centimeters; even then some of the salt remained in solution. Chloride and sulphate of magnesium fell down within the same limits but in increasing quantities, and the residual "bittern" contained mainly the chlorides of magnesium and potassium, bromide of sodium, sulphate of magnesium, and chloride of sodium."

This complete series is hardly ever found in geologic deposits, and it can be assumed that in most cases where it is incomplete, there probably was an interruption and cessation of deposition from various causes. The gypsum deposits of Nova Scotia are generally found in a fairly pure state not necessarily associated with other evaporites, although there are very thin layers of limestone within the more massive gypsum beds. However, the experimental evaporites listed above simplify the conditions somewhat, for the phase diagram worked out by van't Hoff⁵⁵ at 25°C shows that the following minerals may be deposited: bischofite, sylvite, thenardite, carnallite, glaserite, astrakanite, reichardite, kieserite, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, schoenite, leonite, and kainite. At higher or lower temperatures, some of these may no longer be in equilibrium and others may be deposited.

Usiglio's²¹ experiments on the evaporation of sea water indicated that the order of deposition of salts from ocean water was first iron oxide, followed by calcium carbonate, gypsum, and rock salt. His experiments did not indicate the origin of anhydrite, polyhalite ($K_2MgCa_2(SO_4) \cdot 2H_2O$), kieserite ($MgSO_4 \cdot 2H_2O$), and kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$), as well as the many rarer salts associated with them. One of the main criticisms of his evaporation experiments was a sufficient lack of time for complete equilibrium to be attained, such as is more likely to be attained in natural deposits. Other factors are a lack of changes of temperature during deposition, such as would occur in an evaporite basin, and also changes of both temperature and pressure after deposition and burial.

Van't Hoff's studies of salts, and the conditions of their deposition, were partly theoretical, partly experimental, and partly a study of the Strassfurt salt deposits. By mixing two or more salts in an aqueous solution at a certain temperature and at one atmosphere pressure he studied their solubilities and determined the stable phases of the different minerals deposited after equilibrium was attained. From this he prepared phase diagrams which illustrated his results of the complex reactions that occurred. Diagrams were prepared for temperatures of $25^{\circ}C$ and $83^{\circ}C$. Van't Hoff's studies of calcium sulphate in water led him to the conclusion (found incorrect since then) that $66^{\circ}C$ was the transition point

between gypsum and anhydrite in pure water, and that this was lowered to 30°C in the presence of sodium chloride.

Van't Hoff and Weigert⁵⁶ found that in concentrated sodium chloride solutions, the transition point between anhydrite and gypsum is 25°C , and hence anhydrite would be the stable phase once rock salt deposition started. However, if the temperature dropped below this point gypsum would become stable. Thus, if there were fluctuations of temperature around the transition point, there would be alternations of anhydrite and gypsum.

Brauns²¹ did some experimental work on the crystallization of calcium sulphate and came to the conclusion that in a strong solution of sodium chloride containing magnesium sulphate and calcium chloride, only the hemihydrate or the dihydrate would crystallize out. Vater⁵⁷ conducted experiments in which he found that at ordinary temperatures gypsum, and not anhydrite, would crystallize out even in a saturated sodium chloride solution and in a solution containing 3 percent or more (up to saturation) of magnesium sulphate. He concluded that the experiments of Brauns led to incorrect results because Brauns mistook anhydrite for a rhombic modification of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. He believed gypsum to be dimorphic. Kelley³⁰ and others have since shown that there is but one form of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and this is gypsum.

Grabau²¹ concludes that "under ordinary conditions of evaporation of sea water at low temperatures, gypsum is

formed, while an excess of chlorides such as would be produced by the addition of connate salt to an evaporating basin results in the separation of anhydrite." As for other origins of gypsum, he says that it "may be formed by the subsequent alteration of limestone, as has been frequently observed in limestone regions..... Since beds of limestone may readily be associated with salt in desert regions, the association of secondary gypsum with salt is to be expected." The alteration of limestone to gypsum is usually brought about by pyrite being oxidized to form acid sulphates and having this react with the limestone to produce gypsum. Large selenite crystals, down to a pure white alabaster may be formed in this manner. He cites the conclusion of J. W. Dawson who believed that the gypsum deposits of Nova Scotia were formed thusly, with the sulphuric acid derived from local volcanic sources, such as the Triassic volcanoes. Grabau has also concluded, along with many others, that gypsum is often formed by the hydration of anhydrite. An example in process is at Bex in Switzerland where hydration of anhydrite to gypsum has proceeded to a depth of from 60 to 100 feet. Fresh landslides sometimes carry away the surface gypsum to expose the unaltered anhydrite beneath, and "sometimes pieces of anhydrite are found, altered between the folia, or on the exterior, so that the transition from one to the other mineral can be traced." The reverse process, that is, the dehydration of gypsum to anhydrite in nature is

a less well known process, although Rose,⁴⁶ Stewart,^{47,48,49,50} and others have found pseudomorphs of anhydrite after gypsum. There is no doubt, however, that this reaction can and does occur, and probably more often than is indicated in the literature on the subject. It should produce a change in volume of 38 percent, which would result in collapse and brecciation of the bed, and the formation of a folded or convoluted structure called "enterolithic structures."²² The author and Goodman^{17,18} have noted such structures in the gypsum deposits of Nova Scotia, and they have been observed in the salt and gypsum layers of the New York Siluric salt deposits²¹ and in other localities.

The precipitation of salts from sea water is in general in reverse order to their solubilities and the extent of their saturations. According to Wilder,⁵⁹ under present day concentrations of CO₂ in the atmosphere all calcium sulphate deposits formed by the evaporation of sea water or lake water should contain 0.9 percent of calcium carbonate. However, the concentration of gases in the atmosphere, as well as the concentration of salts in the present oceans must have changed over geologic time, and therefore this amount of CaCO₃ must also be variable. Twenhofel⁵³ believes that as a rule evaporation is usually incomplete and therefore only the less soluble salts are

precipitated before deposition ceases. He points out that mother-liquor salts are not commonly found, and that even sodium chloride deposits are less common than calcium sulphate deposits. If the more soluble salts are precipitated, the chances of their continued preservation in the geologic environment are less likely than the calcium sulphate deposits because their higher solubility makes them more susceptible to later removal by ground water solutions. As Twenhofel points out, the gypsum and anhydrite that constitute all calcium sulphate deposits today may not have been deposited in that form, and that a conversion from one to the other may have taken place. The ability of anhydrite to change to gypsum is well known and is illustrated in deposits in Nova Scotia, Ontario, Kansas, New York, and many other localities. Depending on the temperature, pressure, and composition of the surrounding solutions gypsum may "dehydrate" to anhydrite (usually going through a solution stage first).

A major problem in gypsum deposition is encountered in trying to explain the thick deposits found in many places. Assuming a present day salinity of 3.5%, it would take an enormous amount of sea water to form a deposit several hundred feet thick. For example, to deposit only 0.7 feet of gypsum would require 1,000 feet¹ of sea water, whereas 300 feet of gypsum would require the evaporation of about 425,000 feet of sea water, or a body of sea water 80 miles thick. This,

of course, is completely inconsistent with the known facts, and some other means must be found to account for these thicknesses of gypsum.

There are other problems connected with salt precipitation. In the normal succession of salt deposition, gypsum is generally deposited first, followed by the precipitation of sodium chloride. However, there are many cases known where thick beds of sodium chloride are found without any underlying gypsum or anhydrite (even though gypsum might have been deposited first it could have been altered to anhydrite later on). Conversely, large deposits of gypsum and anhydrite are known without any overlying sodium chloride. All explanations for these relatively thick beds of gypsum or anhydrite include some means of replenishing with fresh sea water that sea water which has already evaporated.

The most commonly accepted and satisfactory explanation is the "bar theory," or some modification of it. Originally presented by C. Ochsénus⁴² who did not agree with the existing idea of repeated floodings of very shallow basins, such as lakes or sounds, the theory presumed that the basin of deposition was separated from the ocean by a bar, the latter practically at the same level as the water surface but yet sufficiently high to act as a barrier and thus prevent complete mixing of the sea water and the basin water. As water was removed from the basin by evaporation

with the resultant precipitation of evaporites, fresh sea water replenished it by coming over the bar, while the more concentrated solutions would sink downwards. It was assumed that climatic conditions were such that evaporation was not offset by the entering of fresh waters through streams directly connected with the basin. As the deposits increased in thickness and "rose" towards the surface, the denser solutions in contact with them, called the residual "bittern," also rose and eventually escaped into the ocean. This accounted for the lack of accumulation of potassium and magnesium salts, although should "the bar have increased in height at just this time, the bittern would be retained in the now closed basin and the deposition of the potassium salts would follow." An example of such a basin is the Gulf of Kara Bogaz, which is separated by a bar on the east side of the Caspian Sea.

It would be expected that the conditions just described would have been very favorable for the formation of fossils, for as the organisms were brought into the highly concentrated waters of the basin they would die and normally sink to the bottom where they would be rapidly buried in the forming evaporite beds. However, such fossils are not commonly found in evaporite beds of geologic age. This, along with the absence of salt above the gypsum, or the absence of gypsum below the salt, has led Branson⁵ to modify Ochsenius' bar theory into a hypothesis that tries

to give a better account of the postulated conditions of deposition. He lists the difficulties that are encountered in the other theories as:

- 1) the large volume of water needed to hold all the dissolved calcium sulphate for the gypsum deposits;
- 2) the lack or rarity of other salts;
- 3) the absence of salt sections on top of the gypsum;
- 4) the lack of impurities in the gypsum;
- 5) the lack of fossils.

There are 1.7488 parts of calcium sulphate per thousand parts of water in normal sea-water, and after this becomes sufficiently concentrated by evaporation precipitation will begin. However, after 1.4 parts have been precipitated out, sodium chloride will start to precipitate rapidly. Thus, only the first portion of calcium sulphate will be available for deposition of pure gypsum (assuming the temperature is below the transition point). For thick gypsum deposits, fresh sea water must replenish that which has already evaporated before the sodium chloride becomes too concentrated; otherwise, the latter will be precipitated. Gypsum beds 40 to 50 feet thick are not uncommon, but are limited in areal extent. For example, the Red Bed gypsum deposits of Wyoming are usually less than a mile square where they are 40 to 50 feet thick, but almost 2000 miles square are covered with 10 foot beds. However, the relations between the thick and thin beds show that the time of deposition was about the

same. Therefore, a considerably greater thickness of water would have been needed above the thicker deposits to lay down their 40 to 50 feet of gypsum, that is, a depression in the order of 9000 feet would have had to be present, but this would demand slopes of 50° or greater and this is clearly impossible in this type of basin. The Wyoming deposits do not contain salt beds associated with the gypsum, nor do they have limestone underlying them. This would not be the case if this was a single enclosed basin, no matter how thick, with sea water evaporating in it. Grabau²² believes that a basin with fresh sea water being added to it over a bar should contain many fossils---this is in evidence today in the Gulf of Kara Bogaz---but thick salt and gypsum beds are usually non-fossiliferous. He also states that streams and wind supply some efflorescent gypsum to interior basins, but if this were the case, sand and other impurities would also be brought in. It is pointed out here that thick gypsum beds are usually quite pure and lack these sedimentary impurities.

Branson's modified bar hypothesis⁵ is as follows. Instead of fresh sea water being added to the enclosed basin, very concentrated solutions are brought in. Assuming an evaporating inland sea of a depth of at least 1400 feet, there would be about 10 feet of gypsum deposited

uniformly along the bottom.* Fresh water is constantly

 * In the example cited earlier (the Gulf of Kara Bogaz on the east side of the Caspian Sea), the gypsum is not deposited uniformly⁵³ but is "deposited in quantity along the shores into the Gulf and for some distance beyond the opening. During the winter months the water is saturated with respect to sodium sulphate, but not the chloride, and at that time deposits of glauberite are made in shallow waters and toward the center...." However, the depth of the water in the Gulf of Kara Bogaz is not over 15 meters deep. The deeper the water, the more uniform might be the deposition.

 being added by incoming streams, but at first it cannot keep up with evaporation. However, eventually the sea will have evaporated to the point where it consists of a number of smaller isolated bodies of concentrated waters, separated by shallow bars, with the outer ones still being fed by the streams and the inner ones being fed by overflow from the outer ones after equilibrium is reached between evaporation of the charged sea water and inflow from the streams. Eventually the outer basins will become filled with sediments, fresh water will enter the inner basins, and gypsum deposition will cease. Compared to the original bar theory of Ochsenius this fits in more with the known facts of thick gypsum deposits, although it requires fairly closely

stipulated conditions which may not be too likely to occur. It accounts for the lack of fossils, which would not be expected in the thick deposits because all life would be killed before actual gypsum deposition when the waters first started to become concentrated, whereas the Ochsenius theory assumes fresh sea water being brought in over the bar and hence constantly bringing in a fresh supply of organisms. Branson accounts for the lack of salt deposited above the gypsum by showing that the fresh water brought in to end the gypsum deposition also dilutes the concentrated brine and prevents salt deposition.

CHAPTER II

EXPERIMENTAL WORK

INTRODUCTION

The author was successful in producing conversions from both the gypsum to the anhydrite and the anhydrite to the gypsum. It was found that the fastest way to detect these changes and make positive identifications was by microscopic examination in the first case, and by differential thermal analysis in the latter case. The birefringence of anhydrite is considerably higher than that of gypsum, and even a few very small particles or crystals of anhydrite can be distinguished when mixed with a quantity of larger grains of gypsum. However, the reverse is not true, and therefore thermograms of the anhydrite samples were prepared and examined for the determinative dissociation peaks. It is to be noted here that in no cases were individual peaks found indicating the presence of hemihydrate alone. Either the thermograms were flat over the 100°C to 200°C range, or dual peaks were found together; the former flat curve represents anhydrite and the latter two peaks represent gypsum, as described later.

To increase reaction rates, all the samples consisted of grains that would pass through a 325 mesh screen.

It was found this produced a fairly uniform grain size, although no attempt was made to eliminate the fines. Another reason for using this size range of grains was that they produced low order gray for gypsum under crossed nicols in the microscope, making them markedly different from the anhydrite grains of the same dimensions which showed higher order interference colors. Special care was taken in preparing the samples in an agate mortar and at periodic intervals they were examined for impurities and particularly for any grains of the opposite calcium sulphate form, that is, for particles of gypsum in the anhydrite powder or vice versa. Although no chemical analyses or spectrographic analyses were made, microscopic and differential thermal analysis showed no evidence of any impurities whatsoever. Pure distilled water was used in preparing the saturated calcium sulphate solution that surrounded the sample in each bomb. At the pressures and low temperatures used for the determinations, there was no indication of any reaction between the solution and the stainless steel material that made up the bombs and the sample holders.

MICROSCOPIC EXAMINATION

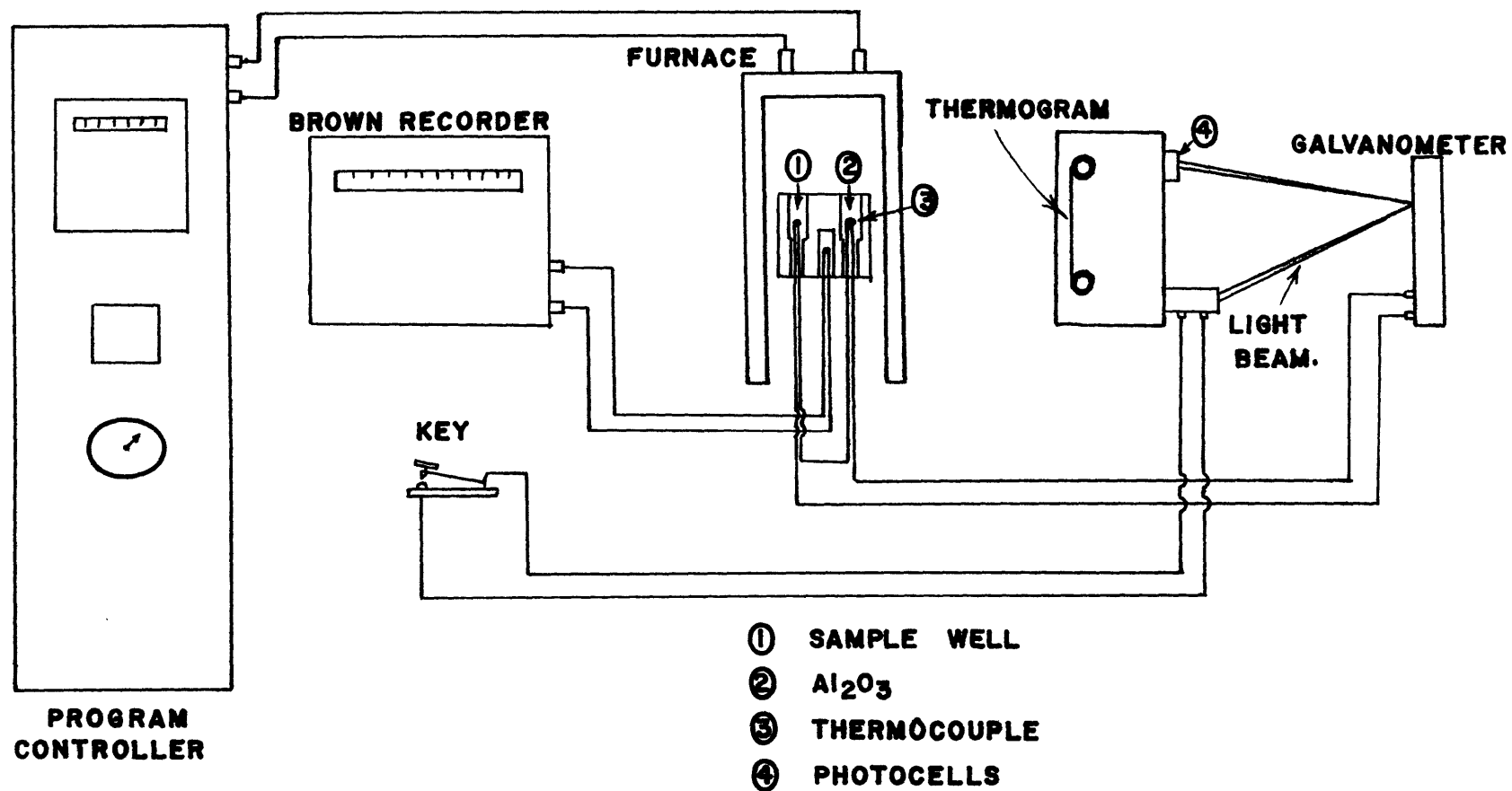
The ability to distinguish gypsum and anhydrite is an essential part of this investigation. Fortunately, they are sufficiently dissimilar to be readily identified, and

several methods were used for their identification. Gypsum is monoclinic, biaxial, optically positive, and has the following indices of refraction:⁹ $n_{\alpha} = 1.520$, $n_{\beta} = 1.523$, $n_{\gamma} = 1.530$. Its birefringence is weak ($n_{\gamma} - n_{\alpha} = 0.010$). It has a perfect cleavage parallel to (010), an imperfect conchoidal cleavage or fracture parallel to (100), and a fibrous cleavage or fracture parallel to ($\bar{1}11$). It has extinction angles of 0° , 13.5° , or 37.5° and is usually white in color. Anhydrite, on the other hand, is orthorhombic, biaxial, optically positive, and has the following indices of refraction: $n_{\gamma} = 1.571$, $n_{\beta} = 1.576$, $n_{\alpha} = 1.614$. Its birefringence is strong ($n_{\gamma} - n_{\alpha} = 0.043$), and it has a pseudocubic cleavage parallel to the three pinakoids (001), (010), and (100). The difference in birefringence and cleavage often is sufficient to distinguish between gypsum and anhydrite in thin sections or in powder samples.

DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis measures the heat evolved or absorbed by a substance as its temperature is changed. The equipment used for measuring differential thermal effects consists of a nickel crucible with three cylindrical wells in it, each containing an iron-constantin thermocouple. One thermocouple leads directly to a Brown Recorder that measures and records the temperature on a scale from 0°C to 1000°C on a continuous strip of graph

paper. The other two couples are located in the remaining two wells, as indicated in Figure 16, and are connected in series but opposed to each other. Their difference in potential is measured by a reflecting galvanometer which reflects a beam of light between two photocells. These follow the beam as it swings back and forth according to the varying voltage, and automatically records the variations with an attached pen on a continuous strip of recording paper. This arrangement is extremely sensitive and can easily measure and record the thermal characteristics of a sample of gypsum as small as one milligram. However, for a full scale reading, 25 milligrams of sample were used when pure or fairly pure samples were being analyzed. If the sample was anhydrite with a very small amount of gypsum present 100 to 200 milligram samples were used to increase the sensitivity. A Leeds and Northrup Micromax program controller was used to operate the small wire-wound electric furnace which surrounds the nickel crucible. Unless otherwise specified, all the samples were heated at the rate of 10°C per minute. This was found to be the ideal rate since higher rates of heating tended to produce narrow sharp peaks, but with a greater lag between the temperature of the nickel block and the temperature of the sample, whereas lower rates of heating tended to produce shallow broad peaks and increased the time required for an analysis. Although the temperature was recorded on a continuous paper



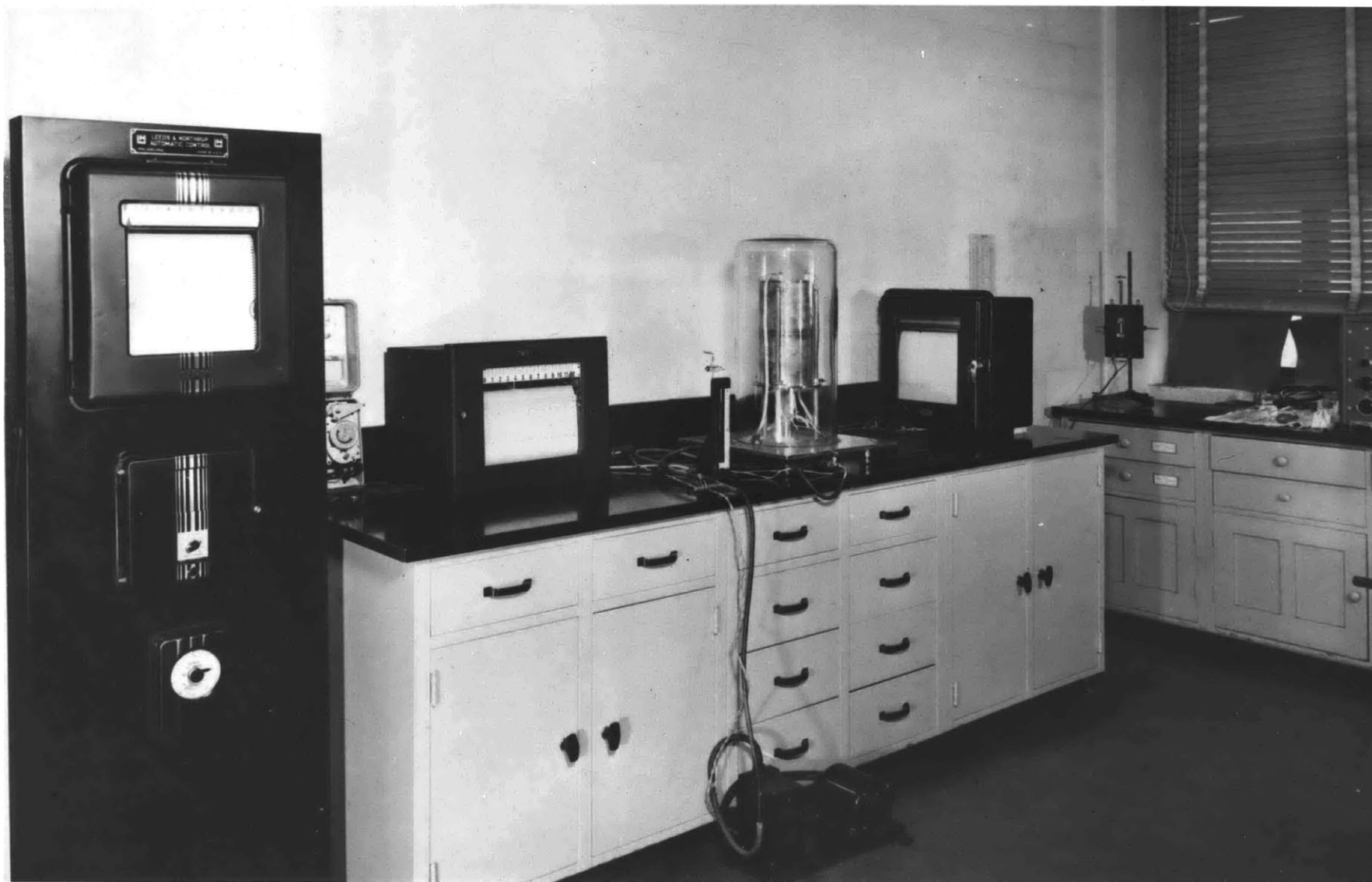
DIFFERENTIAL THERMAL ANALYZER

FIGURE 16.

strip, this was done only as a measure of the linearity of the temperature rise. Direct recording on the thermogram was done by means of the closing of a key that acted as a switch and turned on a light momentarily near the galvanometer. This caused the galvanometer to swing very rapidly for a very short time before it returned to its original position, thus marking a line directly on the thermogram. The key was depressed whenever desired by the operator as he watched the temperature scale. Figure 16 is a schematic diagram of the complete layout described above, and Plate 1 is an early photograph of the equipment during an analysis while the sample was under vacuum.

Gypsum is admirably suited for identification by this method of analysis because it is readily broken down and transformed with the application of heat. From room temperature to 400°C there are two major endothermic reactions and one smaller exothermic one. Anhydrite, on the other hand, is thermally inert over this temperature range, as far as differential thermal effects are concerned. Thus, it does not exhibit any exothermic or endothermic reactions and yields only a straight line with no peaks on a plot of temperature versus time. Figure 17 shows a typical corrected straight line plot for an analysis of pure anhydrite. Below this is a typical three-peaked gypsum curve. With smaller amounts of gypsum Peak C is usually not detected.

PLATE I
EQUIPMENT USED FOR
DIFFERENTIAL THERMAL ANALYSIS



One of the original objectives decided upon when this study was first undertaken was to try and determine what the original composition and structural form of the calcium sulphate was when it was first deposited. Since then, a more basic approach as to what the actual mechanics of deposition are, and particularly what physicochemical postdepositional changes occur, seemed to be more important and would be an aid to the solution of the original problem anyway. However, for the former study it was decided to make a series of analyses of different samples of gypsum taken from a group of gypsum beds distributed over Nova Scotia. The quickest and easiest method was to run each sample through the differential thermal analyzer which, it was hoped, would give the relative amounts of gypsum and anhydrite in each sample.

For this, each sample was quartered, ground in a mortar and pestle, and brought to a standard size by passing it through a 175 mesh sieve and retaining it on a 325 mesh sieve. A 25 milligram portion of the powder was then carefully weighed out and placed around the thermocouple in the sample well, with inert Al_2O_3 packed below and above the sample. All the runs were made at the rate of 10°C per minute and in each case was handled in a similar manner so as to maintain a high degree of reproducibility. As a standard, a sample of pure selenite was prepared in exactly the same way as the gypsum, and a thermogram prepared.

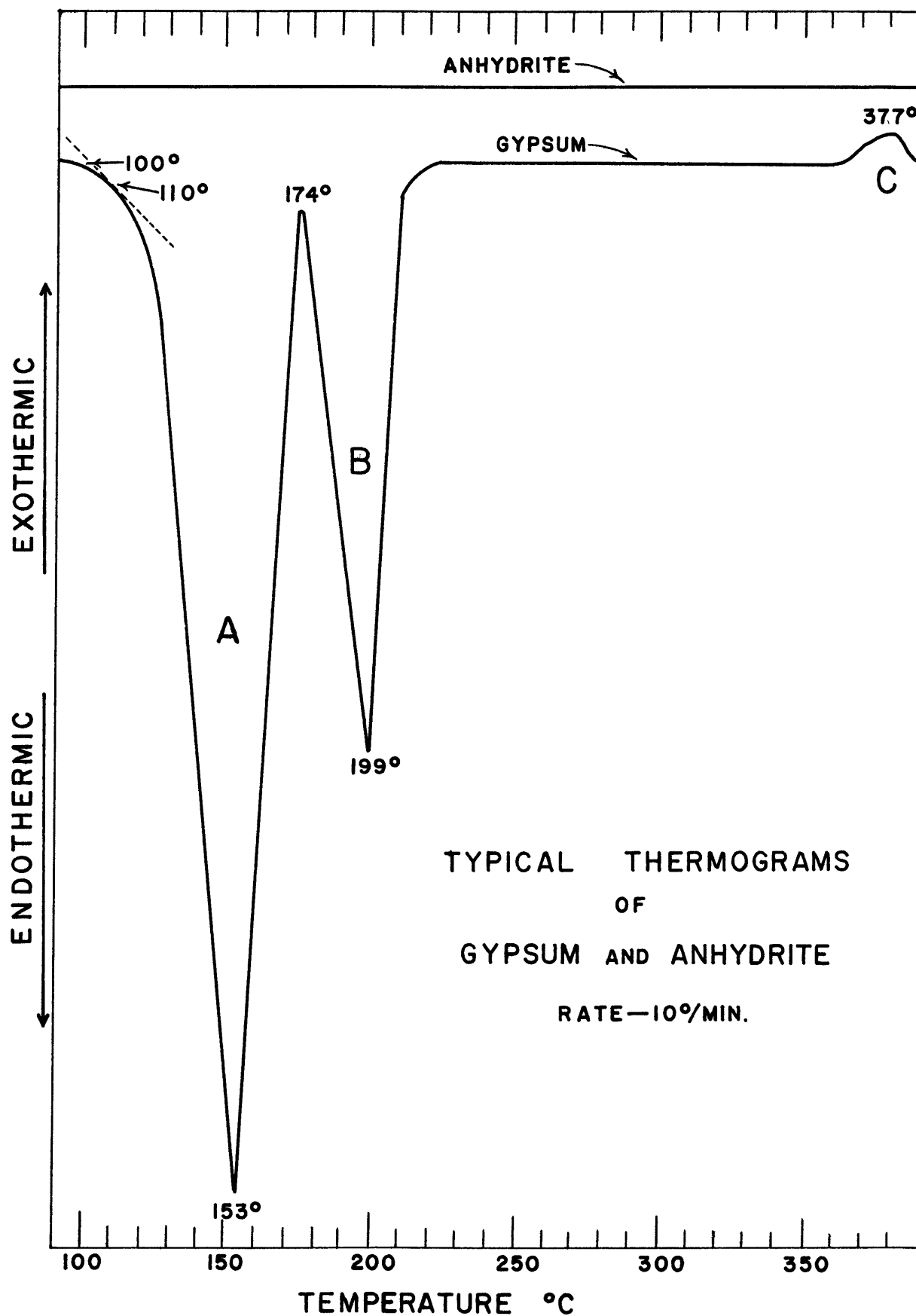


FIGURE 17.

The results of this study are partially listed in Figure 18. Curves A through J represent thermograms of samples taken from a quarry face near Little Narrows, Nova Scotia, with a vertical spacing of 1.5 feet. Care was taken in removing the samples from the quarry face, and exposed surface crusts were avoided. All the curves are similar in shape, location and size of peaks, and size of area under each peak. The areas were measured with a planimeter and results are given in Table 6. Table 6 also lists the points at which the peaks occur and the points at which they first start, the latter being measured by applying a 45° tangent line to the curve, according to the method used by Murray, Fischer,⁴⁰ and others. These results are very close to one another and are within the bounds of experimental error. Curve A, taken as representative of the group, was re-plotted on Figure 19 along with other thermograms representing samples taken from quarries near Antigonish and at Dingwall and Walton, and from cores at South Side Harbor and Dutch Settlement, all in Nova Scotia. Table 7 lists the measurements taken on the curves. As before, there is a great similarity here, indicating that the samples analyzed have compositions consisting almost entirely of pure gypsum. Because of their great similarity, both in physical appearance and in chemical properties, it was decided that differential thermal analysis was not the tool that could be used to distinguish different samples of gypsum, if actual differences really existed among these samples.

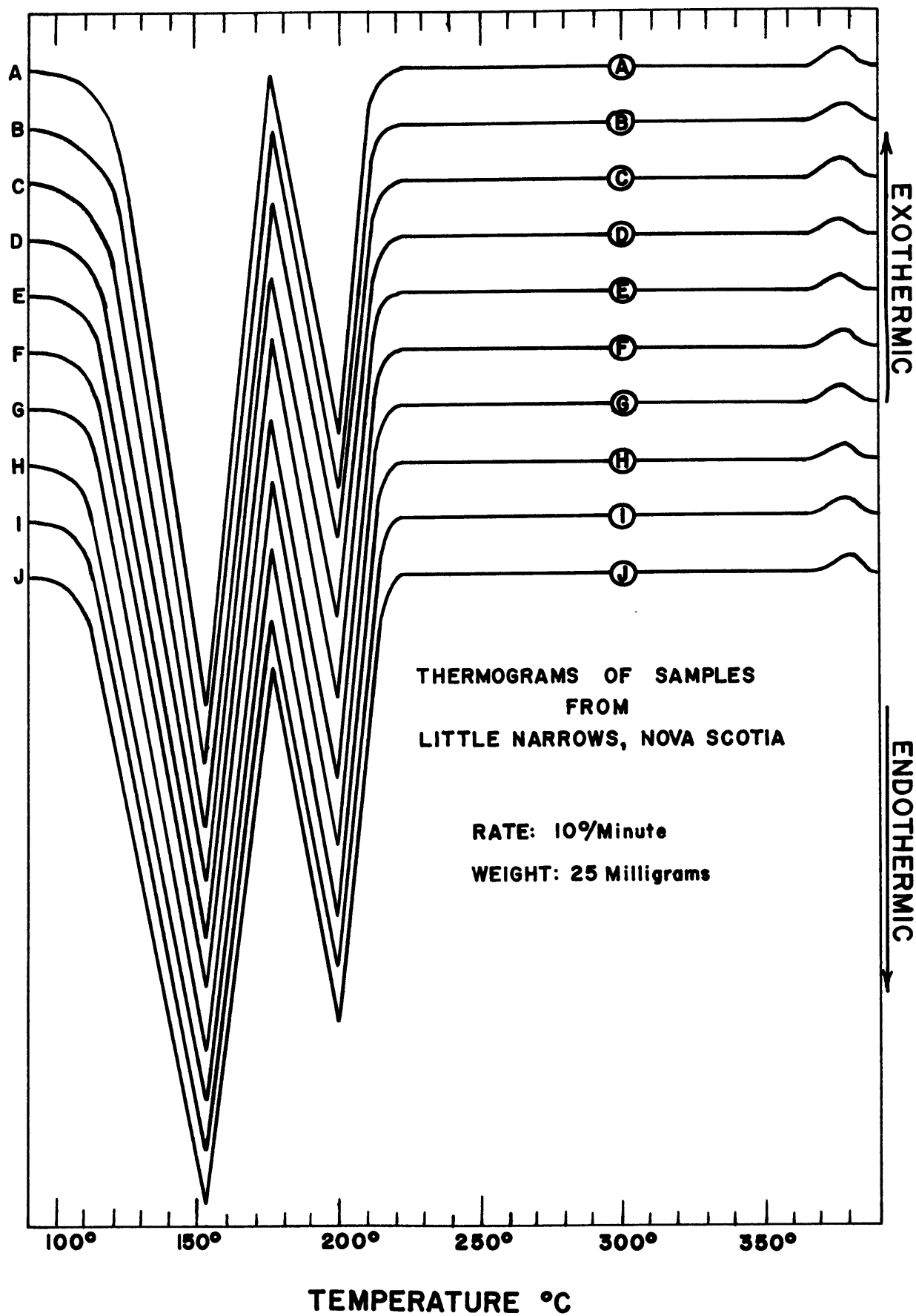


FIGURE 18.

TABLE VI
DIFFERENTIAL THERMAL ANALYSES
Temperature, °C

Sample	First Break	First Peak	Second Break	Second Peak	Third Peak	Area
A	114	155	176	199	378	275
B	111	152	173	201	375	270
C	110	153	172	199	383	310
D	107	154	172	198	376	285
E	105	152	172	199	377	290
F	112	153	170	196	378	270
G	106	153	174	199	378	290
H	109	152	173	198	378	300
I	111	155	172	200	373	295
J	108	155	174	200	375	310

TABLE VII
DIFFERENTIAL THERMAL ANALYSES
Temperature, °C

Sample	First Break	First Peak	Second Break	Second Peak	Third Peak	Area
Little Narrows	110	149	175	198	375	265
Anti-gonish	108	156	173	200	376	290
Dingwall	105	152	170	199	380	325
Walton	113	153	174	201	375	280
South Side Harbor	111	155	176	200	378	330
Dutch Settlement	110	151	173	198	377	320

EXPERIMENTAL TRANSITION POINT DETERMINATIONS

The major portion of the experimental work in this investigation was taken up with the determination of the transition temperatures and pressures of the conversion of gypsum to anhydrite and anhydrite to gypsum in an aqueous solution. For these determinations the following equipment and instruments were used: high-pressure bombs, furnaces, an oil pump and pressure line connected to the bombs, controls for the furnace and pressure, thermocouples and thermometers to measure the temperature, and a pressure gauge. The specially constructed bombs were made of stainless steel, partly because of the great strength of this material and partly because of its negligible reactivity with sulphate solutions at the temperatures and pressures used in the determinations. Each bomb was connected to the pressure system through a thin metal capillary tube, which could be sealed off with a valve. Plate 2 illustrates one of the bombs along with its connecting capillary tube, and Figure 20 is a schematic diagram of the sealed unit.

Heating of the bombs was done by inserting them in furnaces composed of 2½ inch alundum tubes that were 3 inches in diameter and were wound with chromel wire, the whole unit being surrounded with insulation. They were constructed and are described by Cloke.⁸ The voltage applied to the wire, and consequently its current, was controlled by means of a variac and an automatic controller. A thermocouple inserted

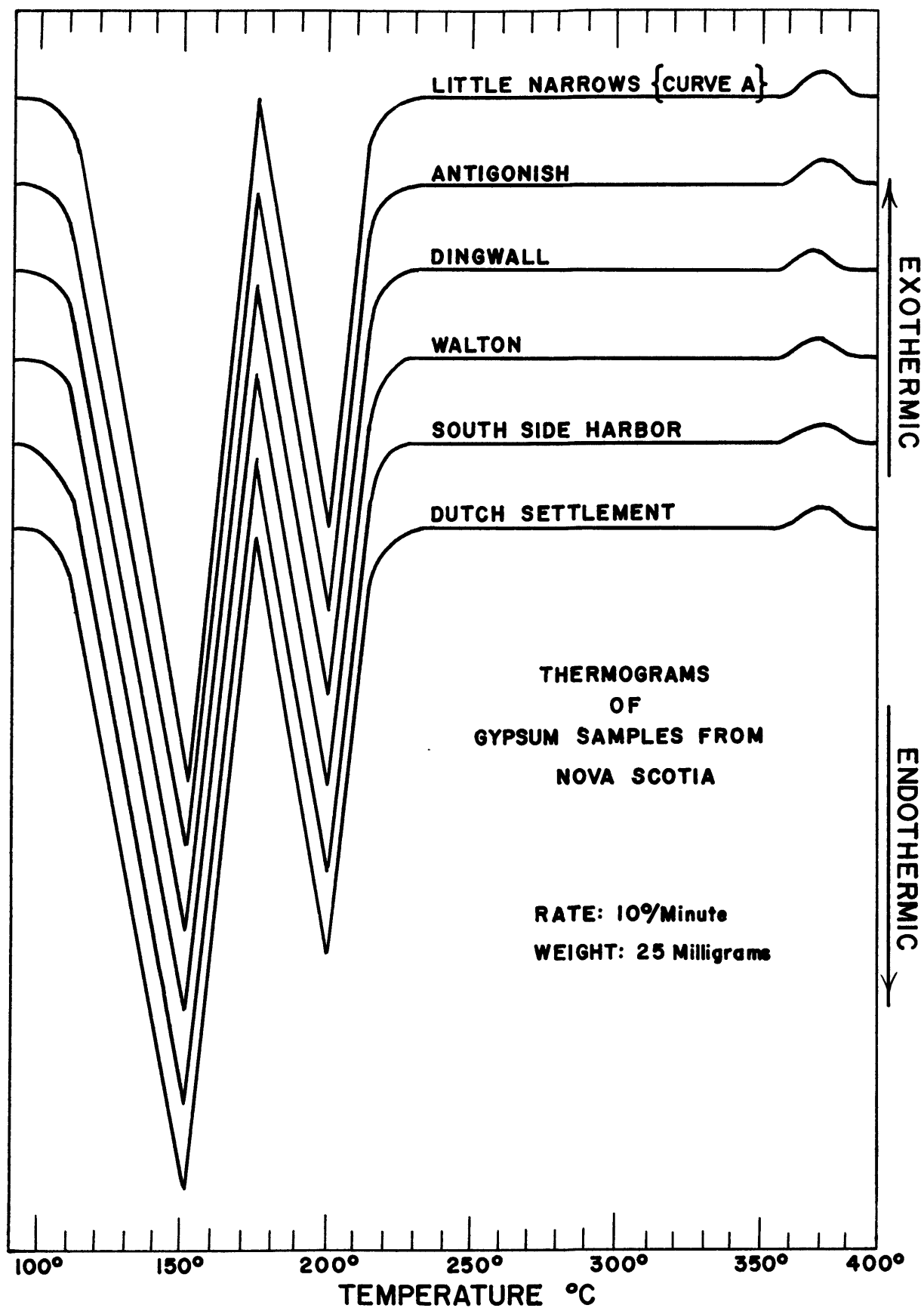
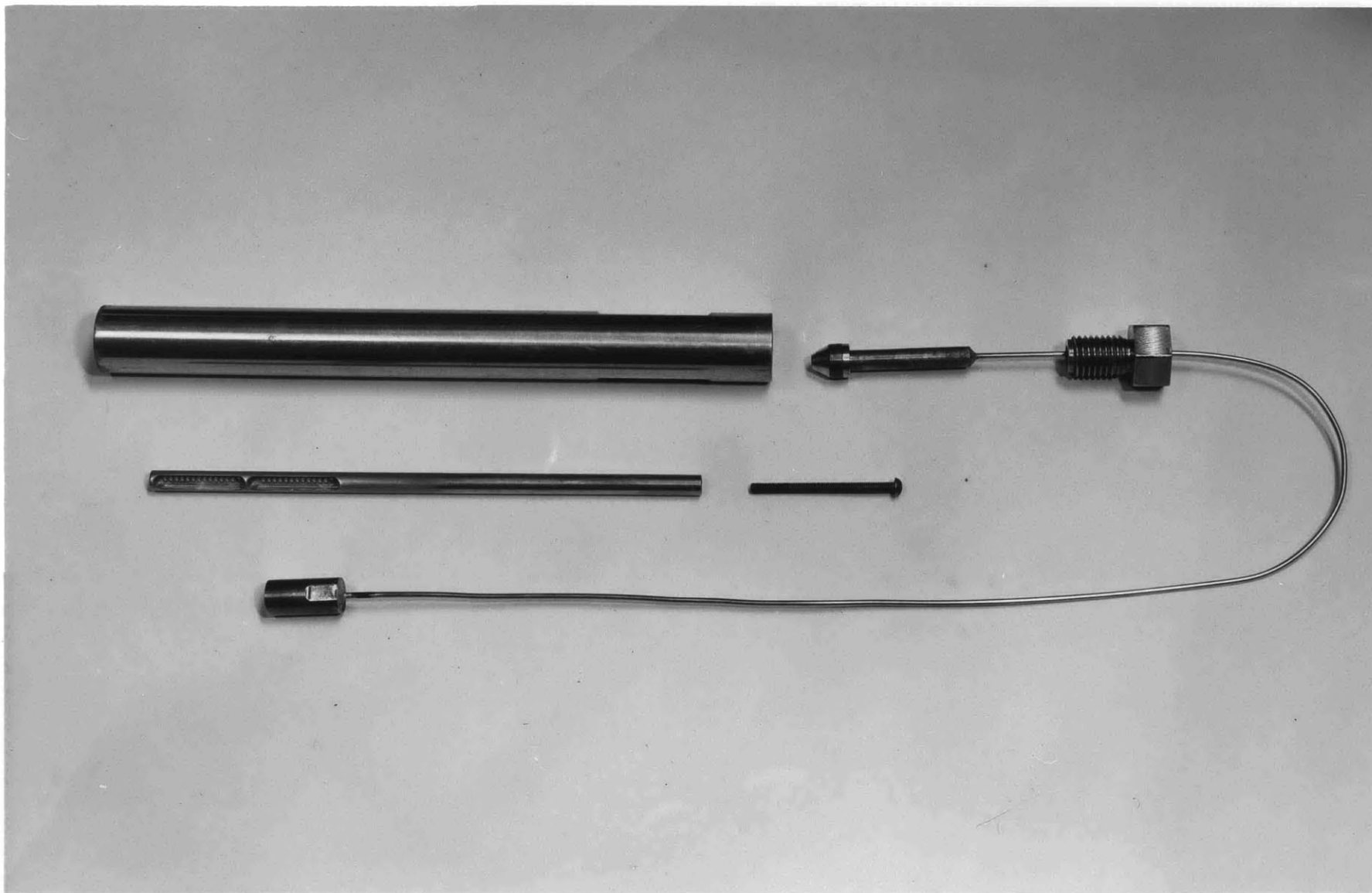


FIGURE 19.

PLATE II

BOMB WITH CAPILLARY TUBING AND SAMPLE HOLDER



in one end of the bomb while it was in the furnace was connected to the controller, and when the desired temperature was reached the current was automatically switched off. For a more accurate temperature determination a thermometer was placed in the furnace adjacent to the bomb. A pressure gauge was connected to the system through a series of valves and was used as a means of measuring the pressure applied to the bomb by the oil pump. A separator, containing oil on the pump side and water on the bomb side, was used to prevent oil from entering the bomb. Plate 3 is a photograph of the complete unit with the pump on the lower right, the furnaces in the center, and the pressure valves and gauge at the top. The furnace on the left contains a bomb during a typical run. At the right is a different style bomb. Figure 21 is a schematic layout of the entire system. Plate 4 shows the complete temperature control panel; the upper left and lower right controllers were used.

The determination of the transition points was done by subjecting a saturated aqueous solution of calcium sulphate containing pure anhydrite or pure gypsum in powder form to a chosen hydrostatic pressure and temperature for a certain length of time, and then examining the pure solid material for any observable changes or conversions. Past work¹⁸ has indicated that both gypsum and anhydrite dissolve very slowly, and that any conversions that take place are

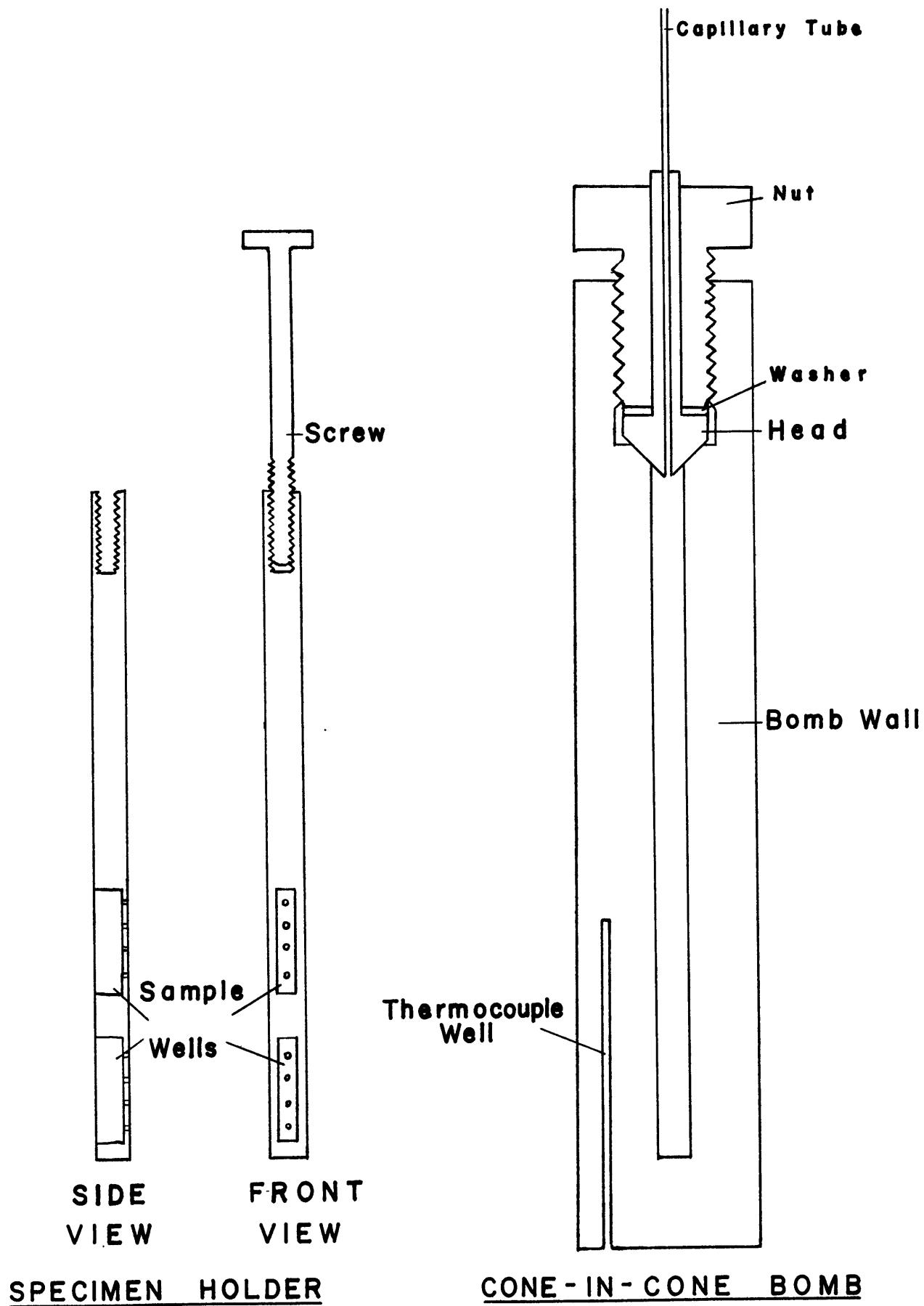
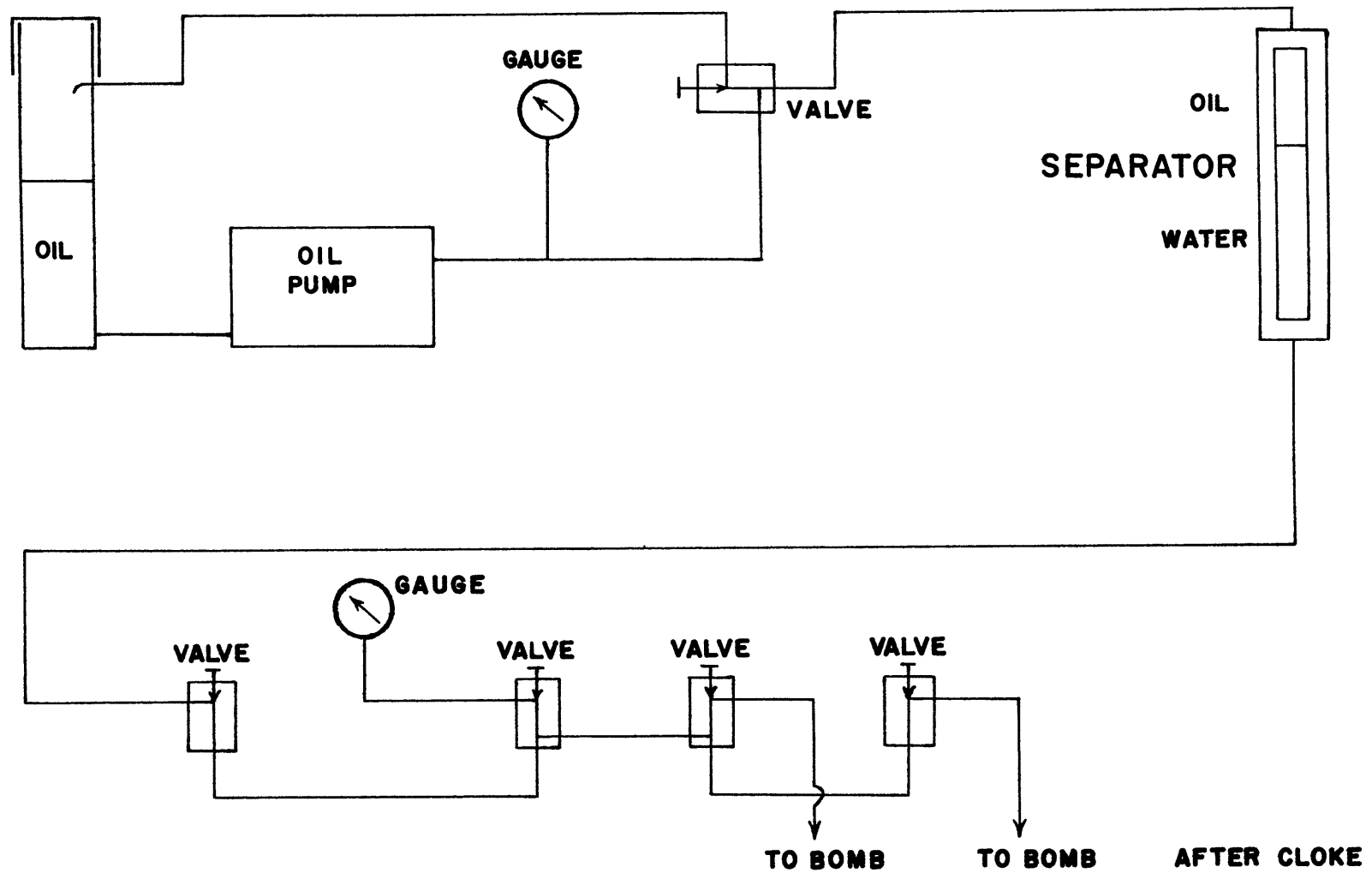


FIGURE 20.

actually reprecipitations of the solid phase after the solution first becomes saturated with calcium sulphate. Therefore, to hasten the normally slow conversion process, a saturated calcium sulphate stock solution was prepared at 25°C and added to the solid dihydrate or anhydrite instead of pure water. A verification of the principle behind this procedure will be discussed later.

It was decided that the best way to determine the transition point at any specific temperature and pressure was to approach that point from both directions, as far as composition was concerned. Therefore, in all the runs, both a sample of gypsum and a sample of anhydrite were placed side by side and tested simultaneously. In each case, they were each carefully wrapped in a piece of platinum foil 0.0015 inches thick and 1-1/2 inches square and kept separate from each other, although they were kept in the same bomb and in contact with the same solution. The solid samples were from the purest natural stones that could be found, the anhydrite coming from a core sample from Little Narrows, Nova Scotia, and the gypsum from the central portion of a large, perfectly transparent selenite crystal from Dingwall, Nova Scotia. These were carefully ground in a porcelain or agate mortar and passed through sieves. Only those particles that passed through a 325 mesh screen were used. The two platinum 'containers', with gypsum in one and anhydrite in the other, were placed in a stainless steel holder (see



PRESSURE SYSTEM

FIGURE 21.

Figure 20 and Plate 2) which was then inserted in the bomb. The latter was filled with the saturated calcium sulphate solution, sealed, connected to the high pressure system, and then brought up to the correct pressure and temperature.

After being maintained there for a specific number of days, the pressure and temperature were rapidly dropped and the samples were removed. To prevent any further reactions from occurring, they were immediately placed in a pure ethyl alcohol bath which removed the free water, and then transferred to an acetone bath to remove the alcohol. After drying at room temperature (25°C) for several minutes, the platinum foil was unfolded and the samples examined.

If a calcium sulphate solution is allowed to evaporate at room temperature, feathery crystals of gypsum will form. For this reason it was imperative to remove all the calcium sulphate solution immediately after the sample was taken from the bomb. Otherwise, gypsum would have been precipitated and the sample would have lost its value. The method of washing in an ethyl alcohol bath followed by a pure acetone bath is described by Fischer,¹⁵ and seemed to be quite effective in removing the free water and thus halting the reaction. As a control, however, it was deemed advisable to check any effect of the alcohol or acetone on the sample. For this, pure samples of gypsum and anhydrite were separately added to a portion of the stock solution of calcium sulphate, soaked for several minutes, removed and

PLATE III

PRESSURE APPARATUS, PUMP, AND FURNACES

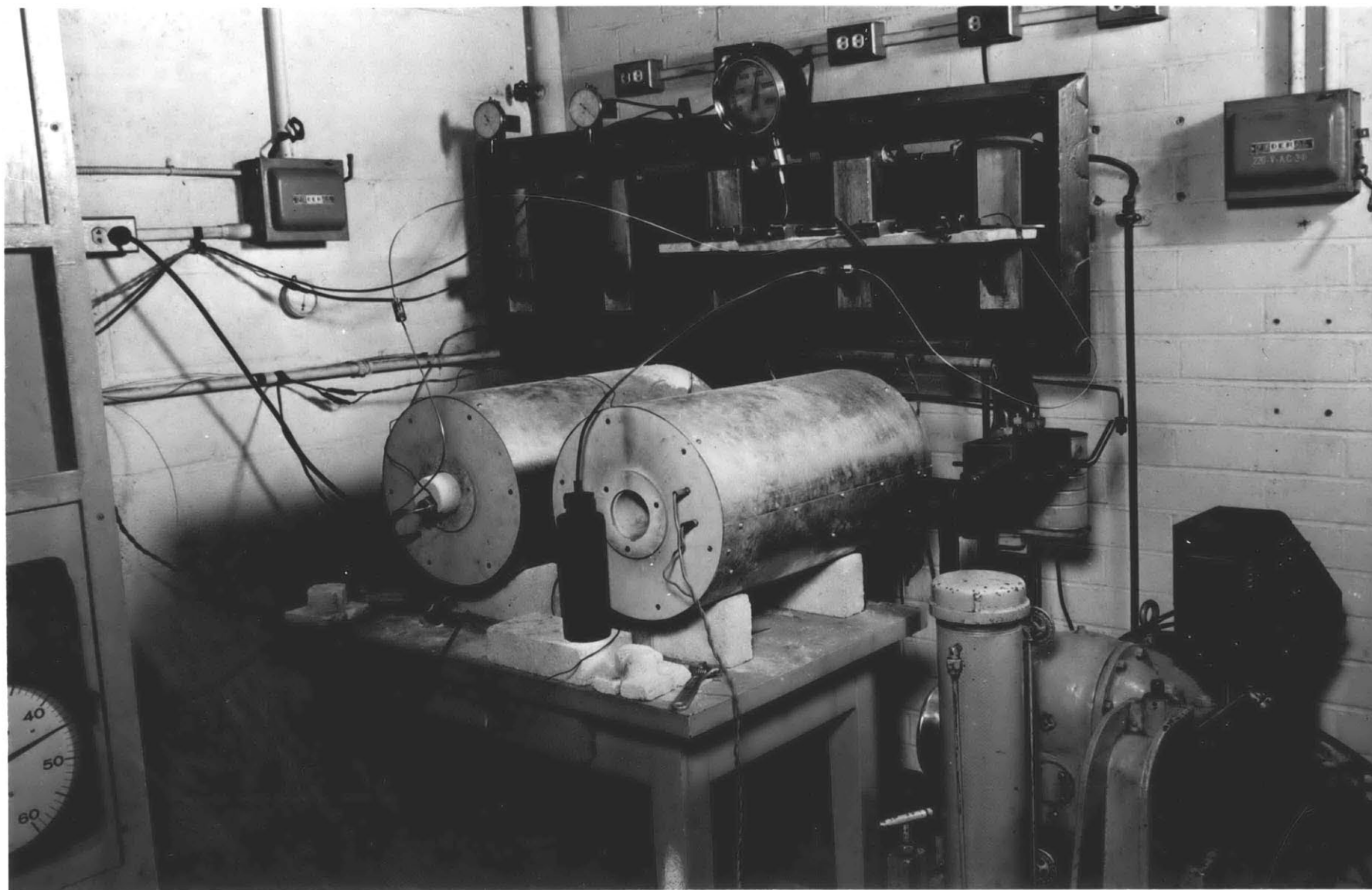
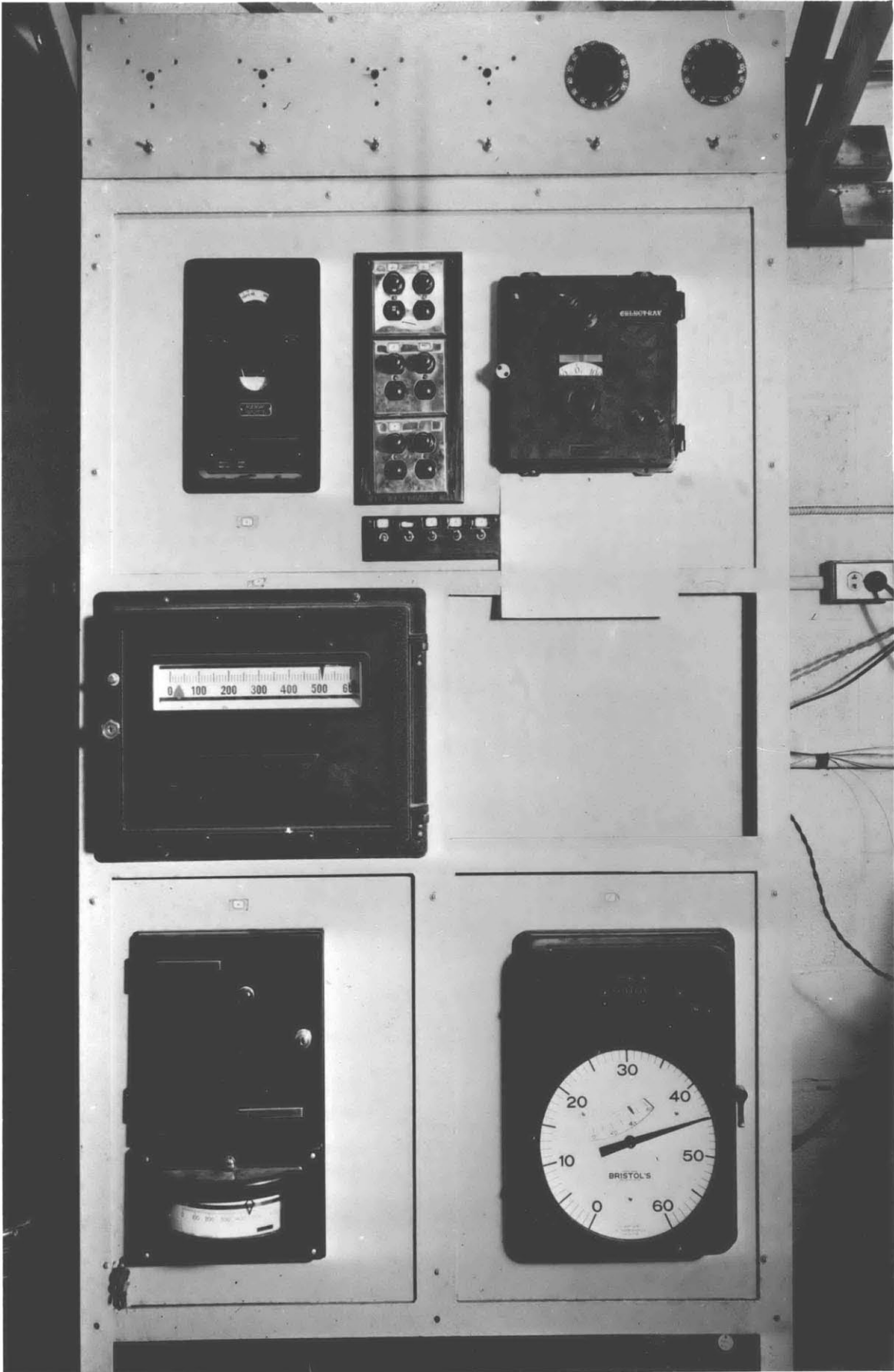


PLATE IV

TEMPERATURE CONTROL PANEL



washed in the alcohol and acetone. After drying, they were examined under the microscope and in a differential thermal analyzer. The results were no different from those analyses of the original pure samples, thus indicating that the addition and then removal of water by this method had no observable effect on the gypsum or anhydrite. It is to be noted, however, that if the calcium sulphate solution was not immediately removed before the sample was dried, some gypsum was precipitated and erratic or misleading results were obtained.

At first, aluminum foil was used in which to wrap the samples, but it was found that a white coating appeared on the pure metal, indicating that some reaction had taken place. To eliminate any such reactions which might alter or affect the normal conversion of anhydrite to gypsum or gypsum to anhydrite, pure platinum foil was used. This was found to be satisfactory.

If a sample of gypsum contained a small amount of anhydrite after being treated experimentally as described above, it was assumed that the temperature and pressure were above the transition point. If the gypsum was unaltered, but the anhydrite contained some gypsum, it is assumed that the temperature and pressure were below the transition point. If neither the gypsum nor the anhydrite were altered, then it is the author's belief that either there was not enough time for the reaction to occur and that

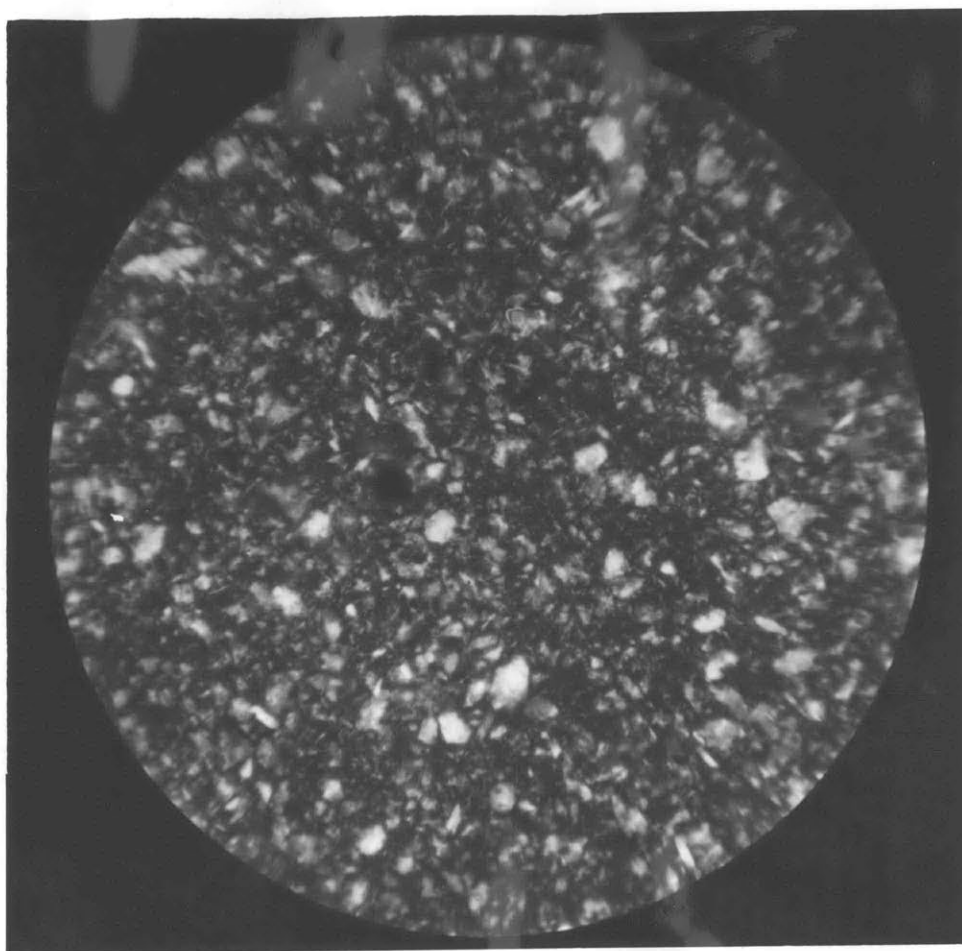


PLATE 5

POWDER SAMPLE OF PURE GYPSUM (60X)

perhaps the solution had not yet reached saturation, or that the pressure and temperature were such that the determination was being conducted exactly at the transition point, a less likely condition. Thus, only a very small change in composition from the original material is here considered to be indicative of a reaction that would fully go to completion if given sufficient time. Although no strong evidence is available as to reaction rates, Kelley's thermodynamic findings, particularly his free energy calculations, firmly show that only the dihydrate and the anhydrite are stable in an aqueous solution. Therefore, any intermediate metastable phase, such as the hemihydrate, will probably not persist for long in the presence of water. Assuming the geologic crystallization and precipitation of the hemihydrate in a lagoonal sea as postulated by Goodman,¹⁸ it is doubtful that this compound, even if it passes through the depositional interface, can survive the very early stages of the diagenetic environment.

The determination of the transition temperature at a specific pressure was done by experimenting with different temperatures at any one pressure. Thus, a number of temperatures were found to be above the transition point, whereas others were found to be below this point. The true point would be between these two ranges.

Plate 6 is a photograph of a sample of gypsum that was left in a saturated calcium sulphate solution at 60°C

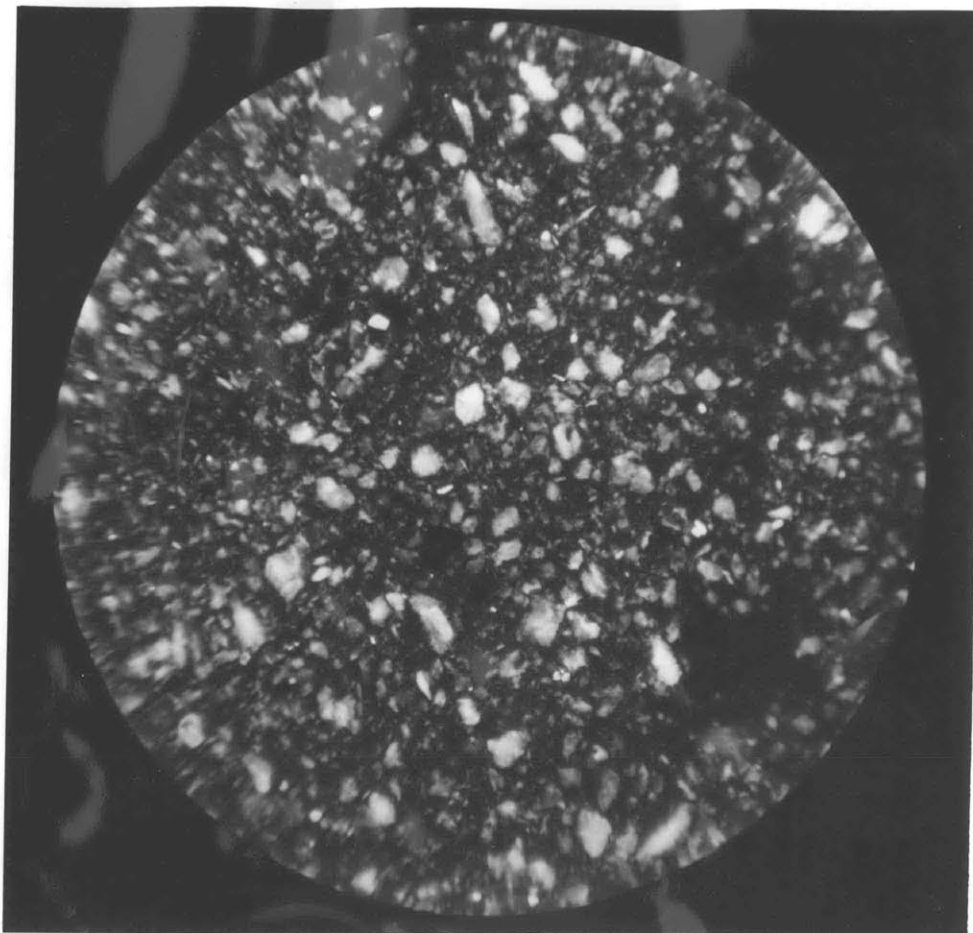


PLATE 6

POWDER SAMPLE OF PURE GYPSUM CONTAINING SMALL
CRYSTALS OF ANHYDRITE
(60x)

and at 500 atmospheres for a period of five days. Upon removal from the bomb it was thoroughly washed with alcohol and acetone and dried at room temperature. Although the majority of the sample is still the original gypsum it is to be noticed that there are now very tiny grains of anhydrite that appear as light-colored particles on the photograph. This is typical of a conversion of gypsum to anhydrite, with new crystals of anhydrite forming above the transition point, but never any observations of any immediate recrystallization of the gypsum grains. This is direct evidence to show the method of recrystallization only after first going into solution. Plate 5 is another photograph showing a portion of the same gypsum sample before it was placed in the bomb. Note the complete absence of any of the light-colored crystals of anhydrite. In many of the tests, the before-and-after analyses and examinations were the same as shown in Plates 5 and 6, when the temperatures and pressures were above the transition point. However, in others the results were not so clear cut, and the distinctions had to be made on the evidence of a few grains that could not be positively identified, but were more representative of anhydrite than of gypsum. This was usually true as the temperatures and pressures became closer and closer to the transition points, which is to be expected since the solubilities of the two substances approach each other and become equal at these points.

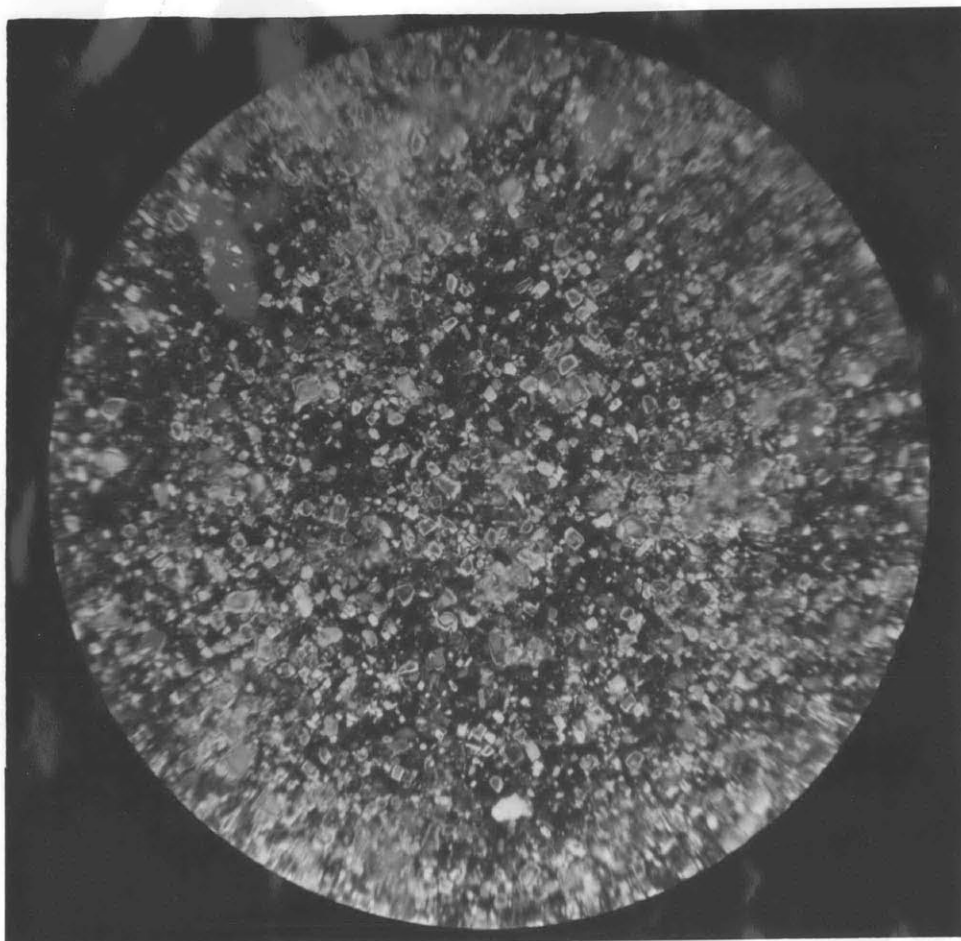


PLATE 7

POWDER SAMPLE OF PURE ANHYDRITE (60X)

The results of the determinations are given in Figure 22 as a pressure-temperature curve. The indeterminate, as well as the questionable and determined points, are given for both the gypsum to anhydrite and the anhydrite to gypsum conversions. A line drawn between these two sets of points is the closest approximation to the transition line.

For most of the points on the approximated transition line, the nearest experimental points that could be considered reliable lie from 3°C to 7°C above or below the line. If more time was allowed for equilibrium to be reached, there is little doubt that this experimental limit could be lowered until positive determinations could be found within the limits of error of the measuring devices alone, which for the equipment used here was plus or minus 1°C . The accuracy of the thermometers was considerably better than this, but the controller and the construction of the furnaces permitted the temperature within the bombs to vary this amount. It is impossible to predict here just how long it would take for equilibrium to be reached when the temperature is within one degree or so of the transition line, but it might run into years, depending on whether the point is reached from supersaturation or undersaturation, the former being more likely to shorten this period of time. For many of the determinations, a period of five days was adequate to start the conversion on its way. For others,

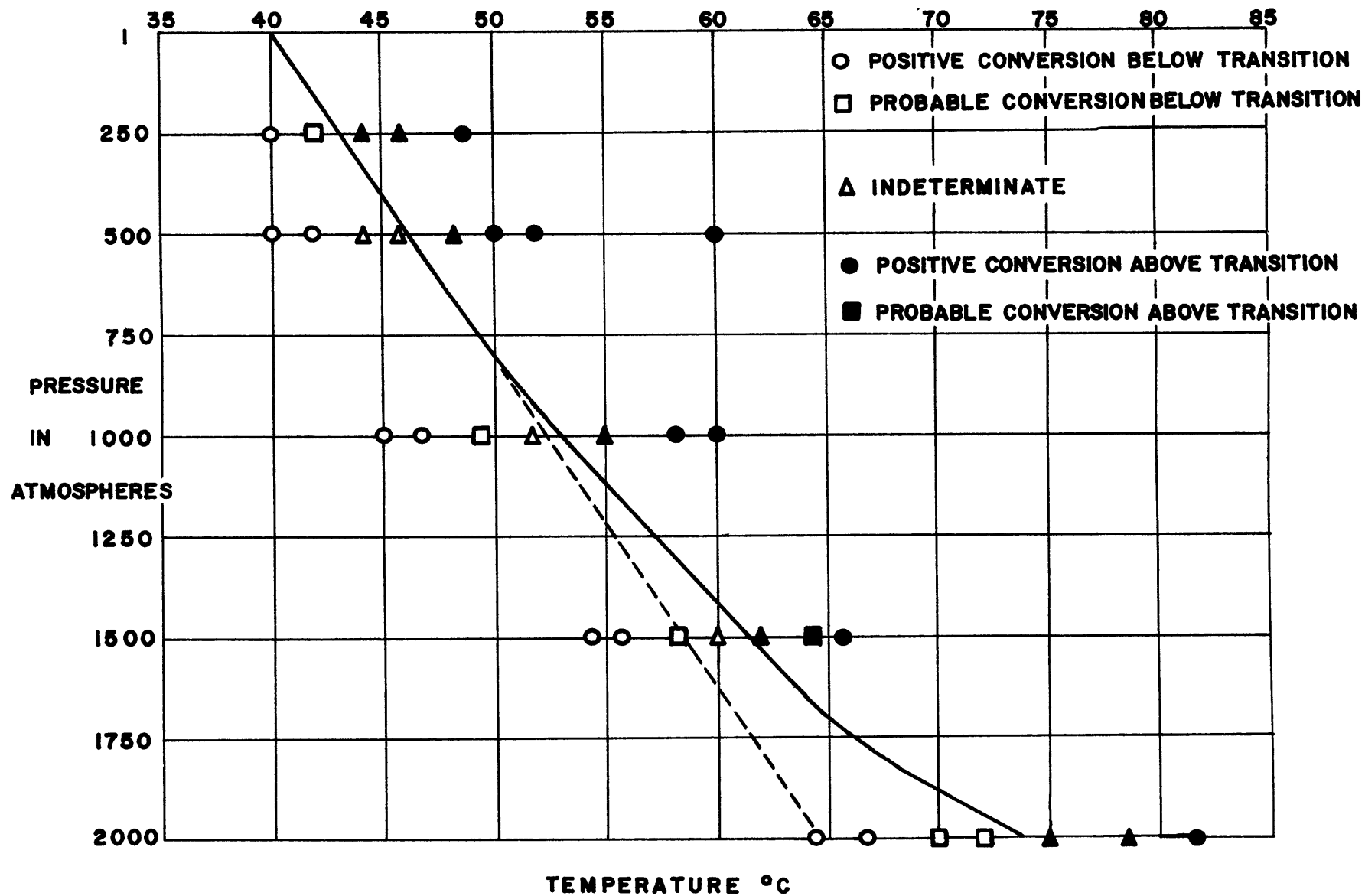


FIGURE 22.

particularly those close to the transition point, periods of twenty days and more were not sufficient. The time for each determination, along with the temperature, pressure, and stable phase are listed in Table 8. These results are plotted on Figure 22 as a pressure-temperature diagram. For a pressure of one atmosphere, a transition temperature of 40°C was plotted, but it was not experimentally determined since it, or 42°C , is already known from previous work. Five pressures were chosen for the actual determinations, namely 250, 500, 1000, 1500, and 2000 atmospheres, and at each of these pressures a set of measurements were made at different temperatures. In all cases, temperatures were chosen so as to find points both above and below the transition. To guide in the choice of such points, MacDonald's plot of this curve from one atmosphere to about 500 atmospheres was extrapolated, as indicated by the dashed line on Figure 22. At 2000 atmospheres, the extrapolated transition temperature is about 64°C . However, there is little doubt that the transition temperature at this pressure is above 64°C , for at 67°C there is a reliable point indicating that gypsum is the stable phase, and therefore the transition temperature must at least be above 67°C .

In all the cases, positive conversions were established both above and below the transition temperatures. However, there is a temperature zone between these limits where conversions either one way or the other could not be

TABLE VIII
CONVERSION DATA

Pressure, Atmospheres	Temperature, °C	Above Transition	Below Transition	In- deter- minate	Time, Days
250	40		X		5
250	42		X(?)		5
250	44			X	7
250	46			X	7
250	49	X			5
500	40		X		5
500	42		X		5
500	44			X	7
500	46			X	7
500	48			X	7
500	50	X			5
500	52	X			5
500	60	X			5
1000	45		X		5
1000	47		X		5
1000	49		X(?)		5
1000	52			X	8
1000	55			X	7
1000	58	X			8
1000	60	X			5
1500	54		X		5
1500	56		X		5
1500	58		X(?)		5
1500	60			X	9
1500	62			X	7
1500	64	X(?)			6
1500	66	X			5
2000	64		X		5
2000	67		X		5
2000	70		X(?)		22
2000	72		X(?)		20
2000	75			X	7
2000	78			X	5
2000	82	X			5

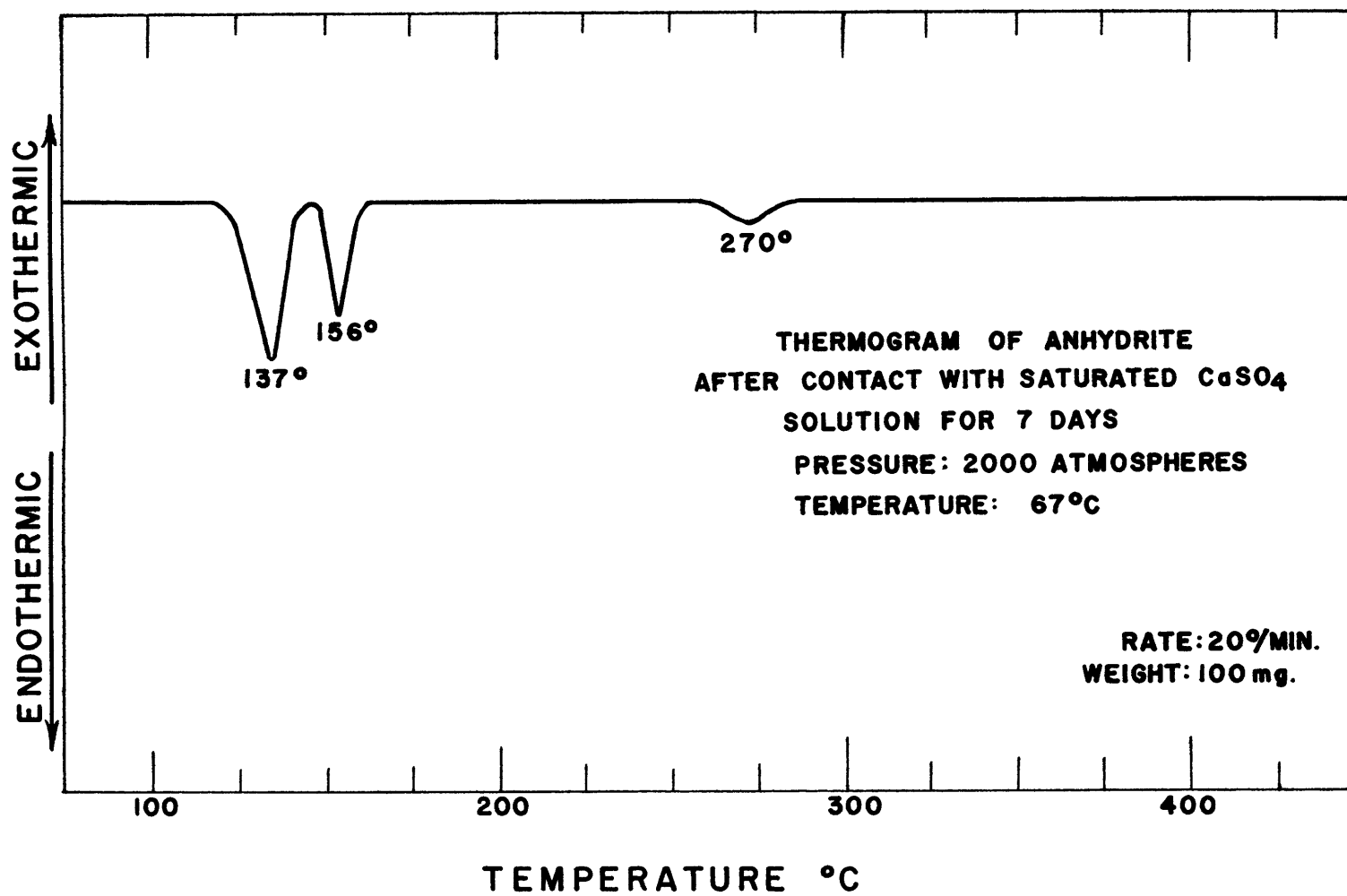


FIGURE 23.

observed, as indicated by the triangles, as well as points where the evidence was not reliable enough to show positive conversions, as indicated by the squares. MacDonald's calculated curve falls well within these limits and although it is possible that his calculations may be off by as much as four degrees at 500 bars, there is little reason for this consideration. The experimentally determined curve corroborates his calculated one as far as it goes, but above 500 atmospheres* there is a definite indication that the

- - - - -
 * MacDonald's pressure units are expressed in bars, whereas the experimental points are expressed in atmospheres. However, for all practical purposes here they can be interchanged, since a bar is 0.98692 atmospheres. At the extreme end of the curve, the difference between 2000 atmospheres and 2000 bars is only about 25 atmospheres or about 1.25%. At lower pressures, the actual difference, of course, is proportionately less.

- - - - -
 transition curve is no longer a straight line but tends to go to higher temperatures.

The factor that causes this divergence from the extrapolated calculated curve might be any one of the assumed constants that, of necessity, had to be included in the calculations since very little is actually known about the behavior of gypsum and anhydrite at high pressures. The calculations are based upon the use of the free energy equation for the reaction:

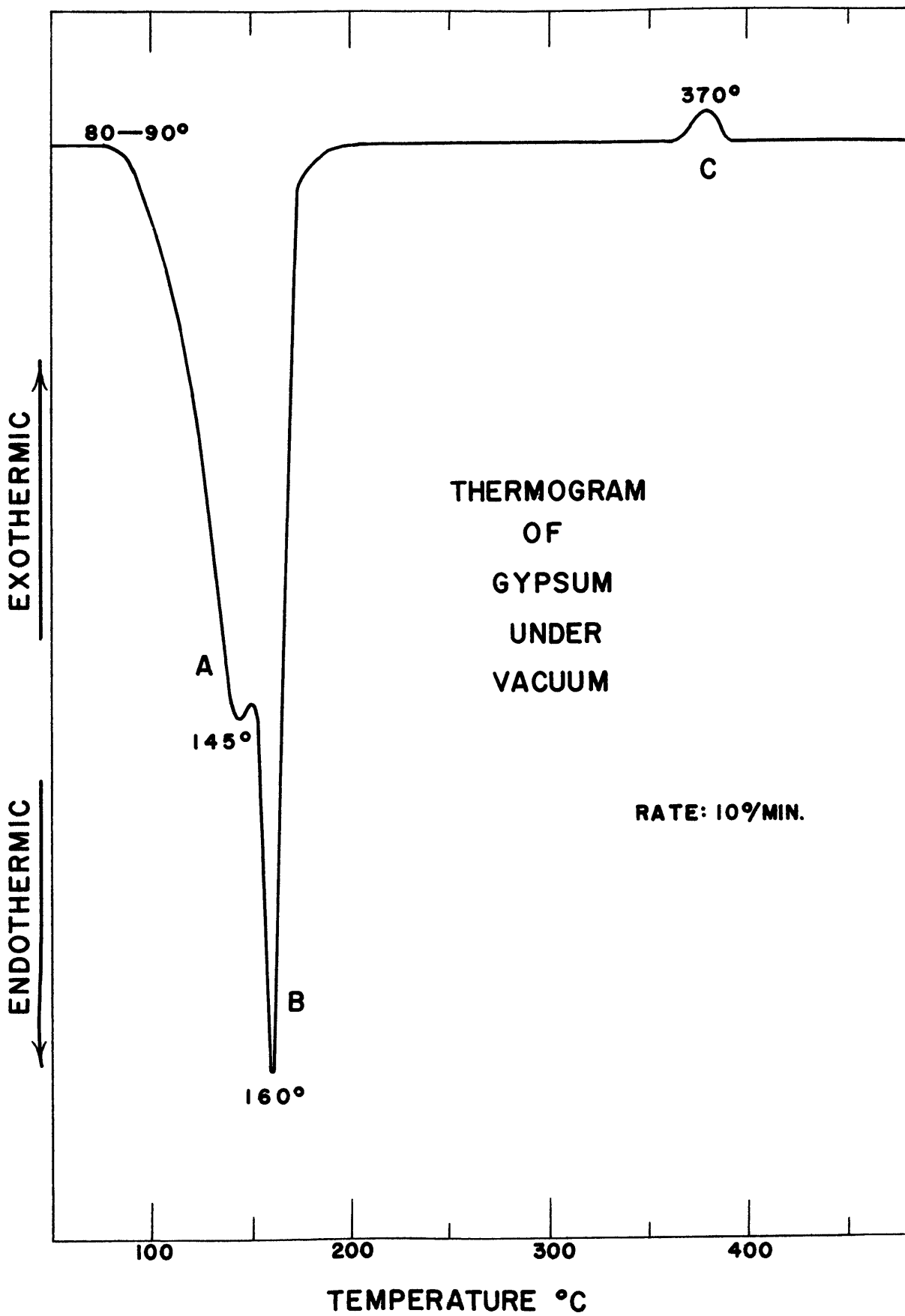
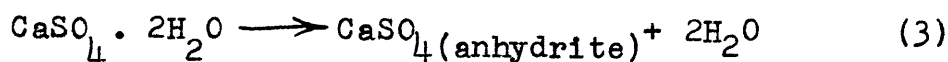


FIGURE 24.



as determined by Kelley³⁰ and his co-workers. This equation is:

$$\Delta G = 163.89T + .0215T^2 - 65.17(T)\log_{10}T - 2495 \quad (4)$$

where ΔG is the free energy of the reaction in calories per mole, and T is in degrees Kelvin. It was found from heat capacity measurements, heats of hydration, and vapor pressure measurements. For the three phases (anhydrite, gypsum, and water) to exist in equilibrium, ΔG must be equal to zero. Hence, $T = 40^\circ\text{C}$ for the free energy equation, and this is the transition point at one atmosphere. MacDonald uses this information to calculate the effect of pressure on the transition, as follows. By partial differentiation, he gets:

$$d\Delta G = \left(\frac{\partial \Delta G}{\partial \Delta P} \right)_T dP + \left(\frac{\partial \Delta G}{\partial \Delta T} \right)_P dT, \quad (5)$$

and since:

$$\frac{\partial \Delta G}{\partial \Delta P} = \Delta V, \quad (6)$$

and:

$$-\Delta S = \left(\frac{\partial \Delta G}{\partial \Delta T} \right)_P, \quad (7)$$

the following can be arrived at after setting $d\Delta G = 0$:

$$\frac{dP}{dT} = \left[\frac{-135.59 - .043T + 65.17\log_{10}T}{\Delta V} \right] 41.84. \quad (8)$$

The constant (41.84) is used to convert entropy units (calories per cubic centimeter) into bars per degree.

MacDonald has assumed that $\Delta V (= 6.66)$ for the reaction

is "constant over the temperature interval 0-50°C and the pressure interval 1 to 500 bars." He then obtains the initial slope at 40°C and considers the transition curve to be a straight line. This slope is:

$$\left. \frac{dP}{dT} \right|_{40^{\circ}\text{C}} = 85.4 \text{ bars/degree}, \quad (9)$$

and at 500 bars the transition temperature is 46°C, plotted as Curve A on Figure 6. This is for equal hydrostatic and lithostatic pressures. For a lithostatic pressure 2.4 times greater than the hydrostatic pressure he uses the following equation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V_s + V_{\text{H}_2\text{O}}/2.4}, \quad (10)$$

"where ΔV_s is the difference in volume of one mole of anhydrite and gypsum, $V_{\text{H}_2\text{O}}$ is the volume of 2 moles of pure H_2O , and P is the pressure on the solid phases.

$$\begin{aligned} \Delta V_s &= -29.48 \text{ cc per mole of anhydrite} \\ V_{\text{H}_2\text{O}}/2.4 &= 15.06 \text{ cc per two moles of water} \\ \left. \frac{dP}{dT} \right|_{40^{\circ}\text{C}} &= -39.45 \text{ bars/degree.} \end{aligned}$$

This result is plotted on Figure 6 as Curve B. Similar calculations can be made for the effect of dissolved salts on the transition temperature.

By examining the above equations it can be seen that there are two factors upon which the strength of the calculations lie, and these are (1) the original free energy

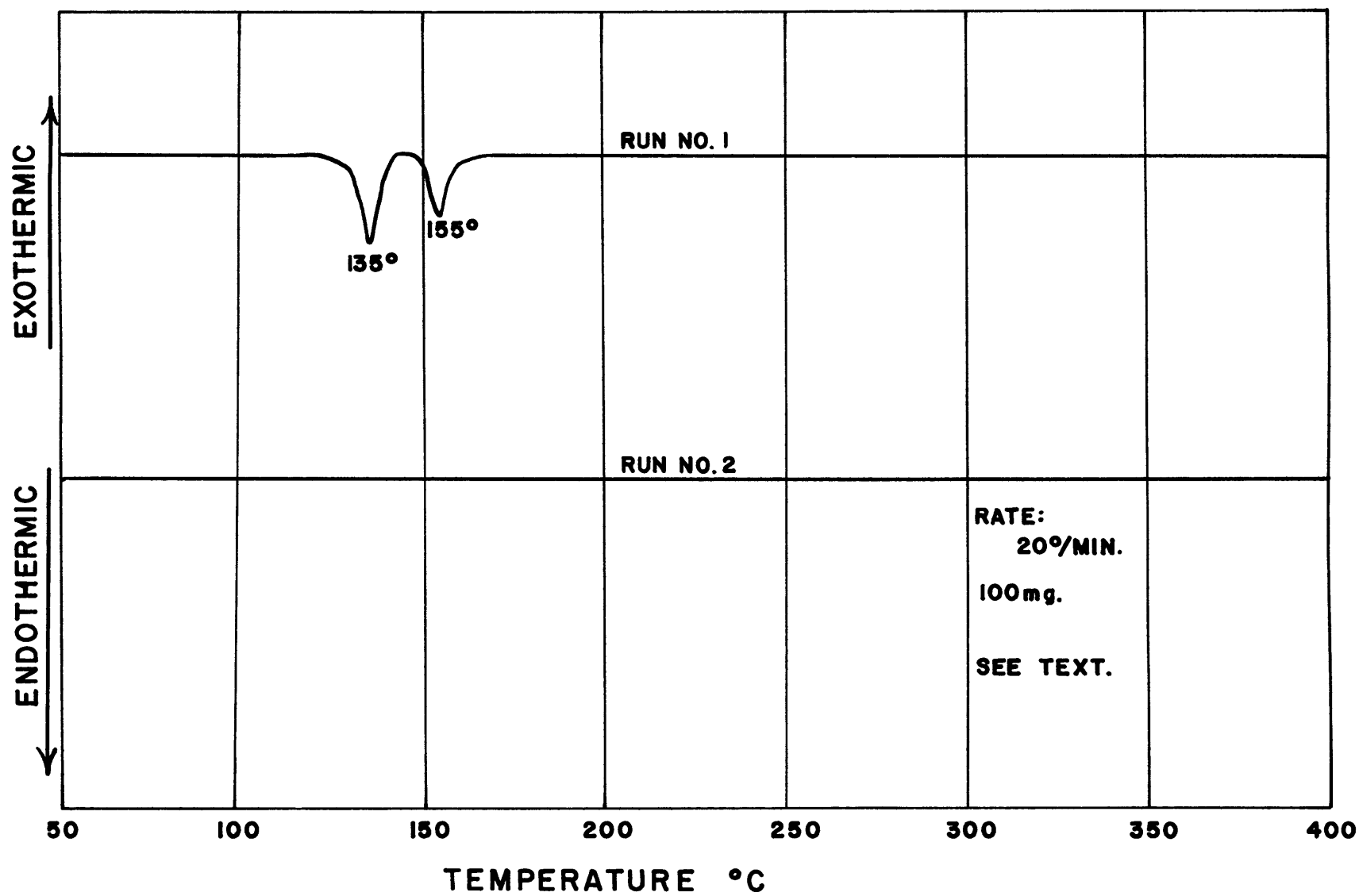


FIGURE 25.

equation which was based on three types of measurements, and (2) the difference in volume (ΔV) for the gypsum-anhydrite reaction, which equals 6.66 cc per mole of anhydrite. However, these measurements were all made at or about one atmosphere pressure, and might be different at higher pressures. It might be expected, for example, that the compressibilities of gypsum and anhydrite would change with increasing pressure. If they changed differentially with respect to each other, this alone would be sufficient to account for the divergence of the experimentally determined transition points from the calculated ones at higher pressures. However, since ΔS will also change with increasing pressure and will tend to balance the change in ΔV , the slope will not be greatly affected. This can be shown by calculating the curvature of the transition curve, that is, $\frac{d^2T}{dP^2}$, which is a small figure.³⁸

NATURE OF THE CONVERSION

A verification of the nature of the conversion, that is, recrystallization of the stable phase after the solution becomes saturated with respect to calcium sulphate was found when a sample of anhydrite was placed in a bomb for five days at a temperature of 38°C and at a pressure of 500 atmospheres, which was well below the transition point. Figure 25, run No. 1, shows the thermogram corresponding to the anhydrite

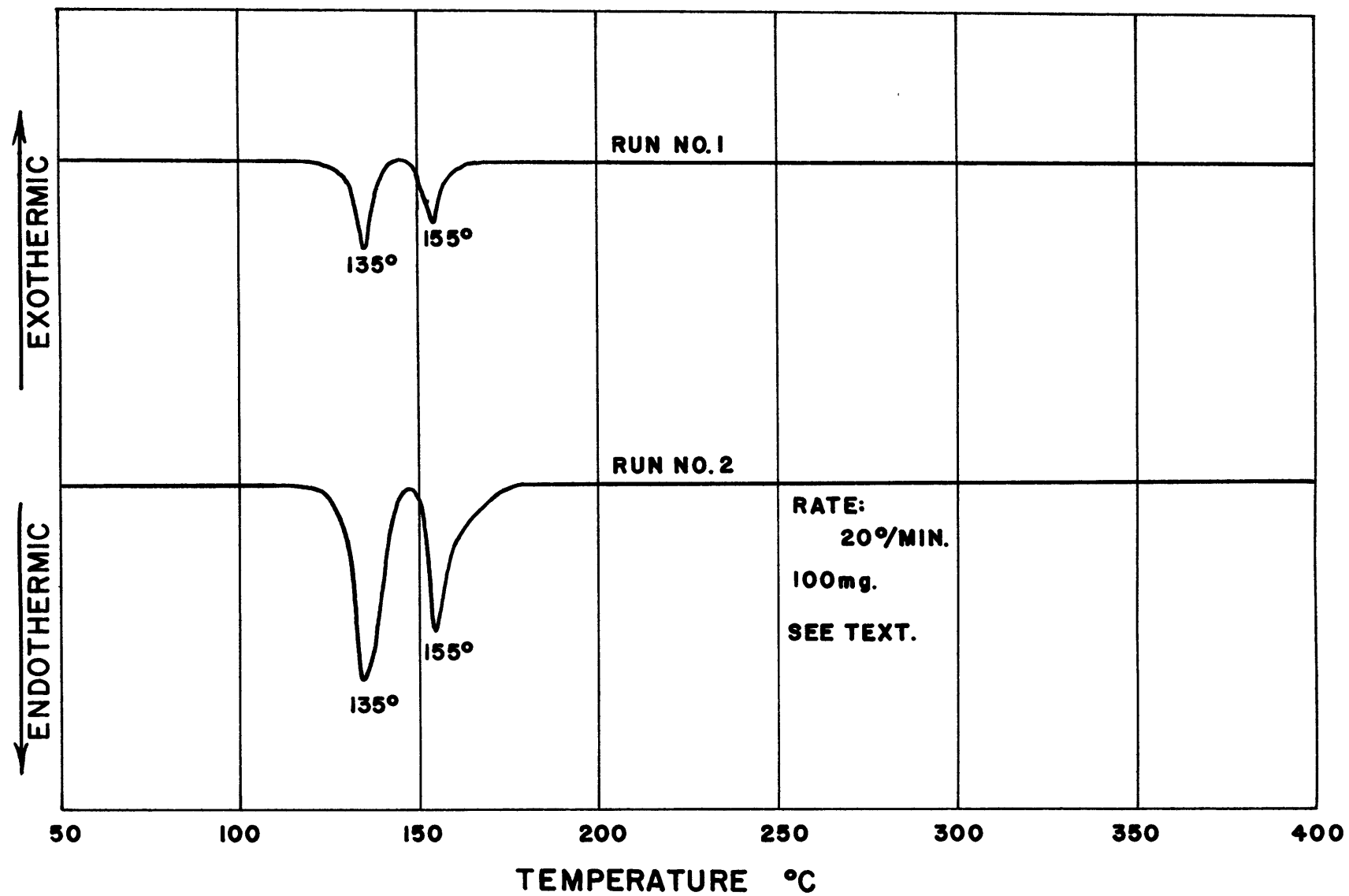


FIGURE 26.

after it was removed, washed in alcohol and acetone, and dried. As would be expected, there are the familiar endothermic peaks corresponding to the two-stage breakdown of gypsum to soluble anhydrite, but for the purpose here, it indicates the definite presence of gypsum. This same sample was then taken and placed in another bomb at the same temperature and pressure as the one above, but instead of surrounding the material with a saturated calcium sulphate solution, pure water was used. After five days the bomb was unsealed and the sample re-examined and analyzed, and is shown as run No. 2 on Figure 25. According to the thermogram, there is a complete absence of any dihydrate, indicating either a conversion back to the anhydrite, or a disappearance of the gypsum. The former is not likely, since we are well below the transition point, and therefore the gypsum must have gone into solution. For the amount of pure water available, and the length of time, the solution did not reach saturation, and all that happened was that all of the previously formed gypsum, plus some of the original anhydrite, went back into solution.

To substantiate the above explanation, the first half of the experiment was exactly duplicated, and a new sample of anhydrite was prepared containing a small amount of gypsum. As before, this was checked by differential thermal analysis, as shown by run No. 1 on Figure 26. The sample was then put back into another bomb, which contained some of the saturated

calcium sulphate stock solution, and left as before at 38°C and 500 atmospheres for five days. When taken out and analyzed (see run No. 2 on Figure 26), the anhydrite contained a larger amount of gypsum than before, indicating that the conversion continued taking place and was, in effect, the same conversion that would have taken place if the sample had been left undisturbed in the bomb for ten days at that temperature and pressure. These experiments would seem to leave little doubt that at least the conversion from anhydrite to gypsum follows Posnjak's⁴⁴ criticism of van't Hoff, and that the recrystallization is not direct but goes through a saturated solution phase first. The fact that the small amount of gypsum present was completely dissolved in the first experiment whereas the anhydrite still remained as the solid phase, can be explained by referring to the phase diagram in Figure 8. At 38°C and one atmosphere the solubility of anhydrite is about 0.216% by weight, which is only slightly more than the solubility of gypsum (about 0.208% by weight) at the same temperature and pressure. From this, it can be seen that the gypsum will dissolve almost as readily as the anhydrite, and it is safe to assume that although the solubilities may be different at higher pressures, the solubility relationship must be quite similar. Thus, all the gypsum dissolved, probably along with some of the anhydrite, and left just pure anhydrite remaining.

HIGH PRESSURE FORM OF CALCIUM SULPHATE

In several of the thermograms of the samples subjected to the highest pressure (2000 atmospheres), a small endotherm at about 270°C was found. This could not have been due to instrumentation effects or to any foreign material in the gypsum and anhydrite samples, for these were carefully checked. The author believes that a new form of calcium sulphate comes into existence at these high pressures and may be either stable or metastable. Apparently, this does not stop the conversions to gypsum below the transition point or the conversions to anhydrite above this point, although it is possible that it affects the transition and causes the curve to decrease its slope, as shown in Figure 22. Other than observing the endothermic peak on the thermogram, no other work was done in studying this new phase, since it was not found in microscopic examination of the pressurized sample. It is possible that X-ray examination might detect it and also give some information as to its crystal structure and chemical formula. Figure 23 is a thermogram showing this endothermic peak on a curve of pure anhydrite containing a small amount of gypsum after the former has undergone partial conversion at a pressure of 2000 atmospheres and a temperature of 67°C .

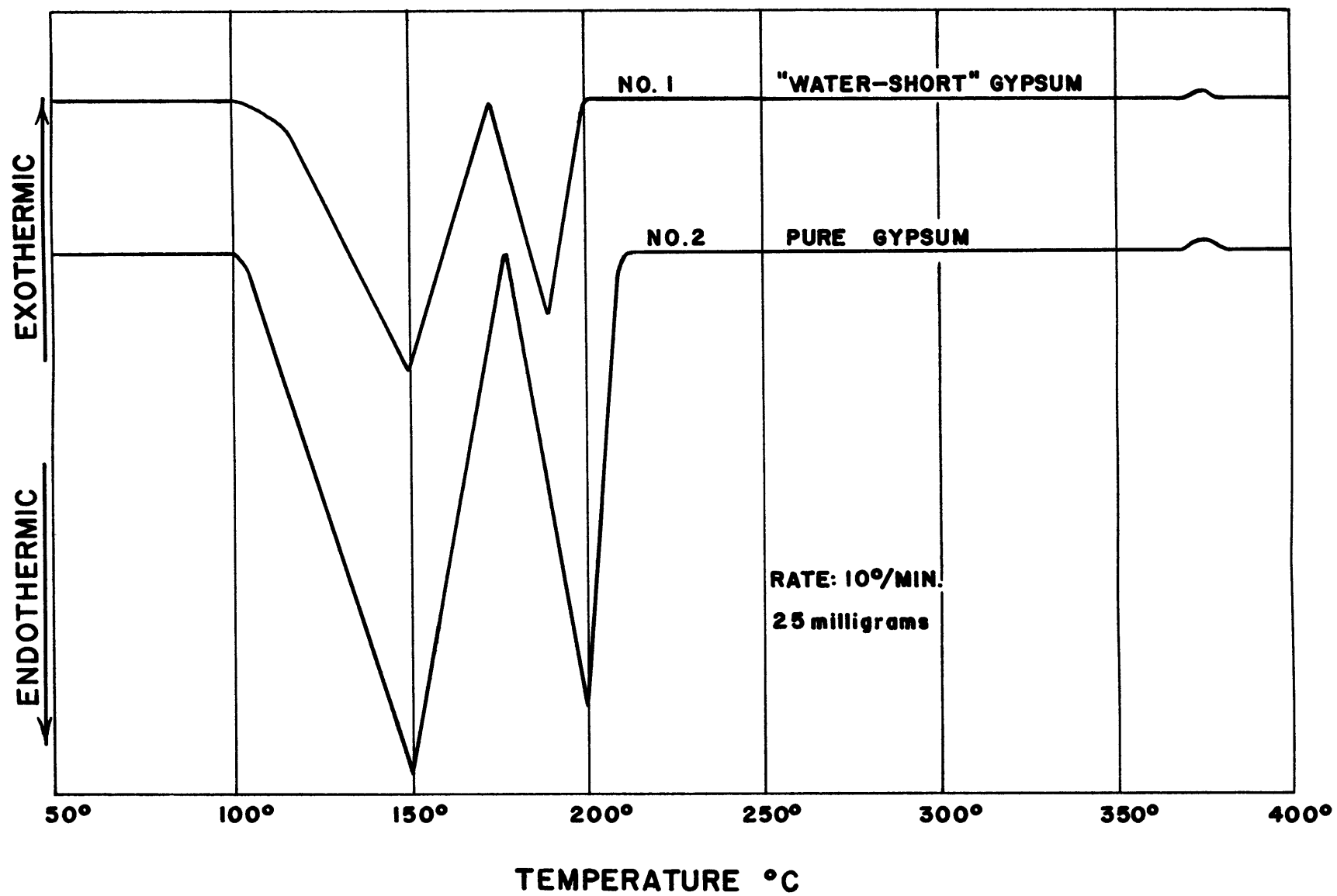


FIGURE 27.

"WATER-SHORT GYPSUM"

In the gypsum quarries of Nova Scotia the expression "water-short gypsum" can often be heard. This refers to the zeolitic type of water-binding, for it is believed by some that this "water-short gypsum" is neither gypsum nor anhydrite but rather some calcium sulphate mineral between the two containing an intermediate amount of water. Several samples of this material were carefully examined in the laboratory, both microscopically and by differential thermal analysis. Under the microscope, both in thin section and in powdered grains, only a mixture of pure anhydrite and pure gypsum were observed. Plate 9 is a photograph of a "water-short gypsum" boulder showing the darker core of anhydrite and gypsum, and the white surface crust of pure gypsum. Plate 8 is a powder sample of the dark material showing the typical anhydrite pseudocubic fracture particles as well as gypsum fragments. The differential thermal analysis curve No. 1 (Figure 27) of this "water-short gypsum" shows the typical dissociation peaks that mark the breakdown from the dihydrate to the hemihydrate and thence to the soluble anhydrite, all endothermic, and then the exothermic peak that marks the change to the insoluble anhydrite. A 25 milligram sample was used for this determination, and if compared with the thermogram of another 25 milligram sample of pure gypsum it can be easily seen that there is a smaller quantity or percentage of gypsum in "water-short gypsum"

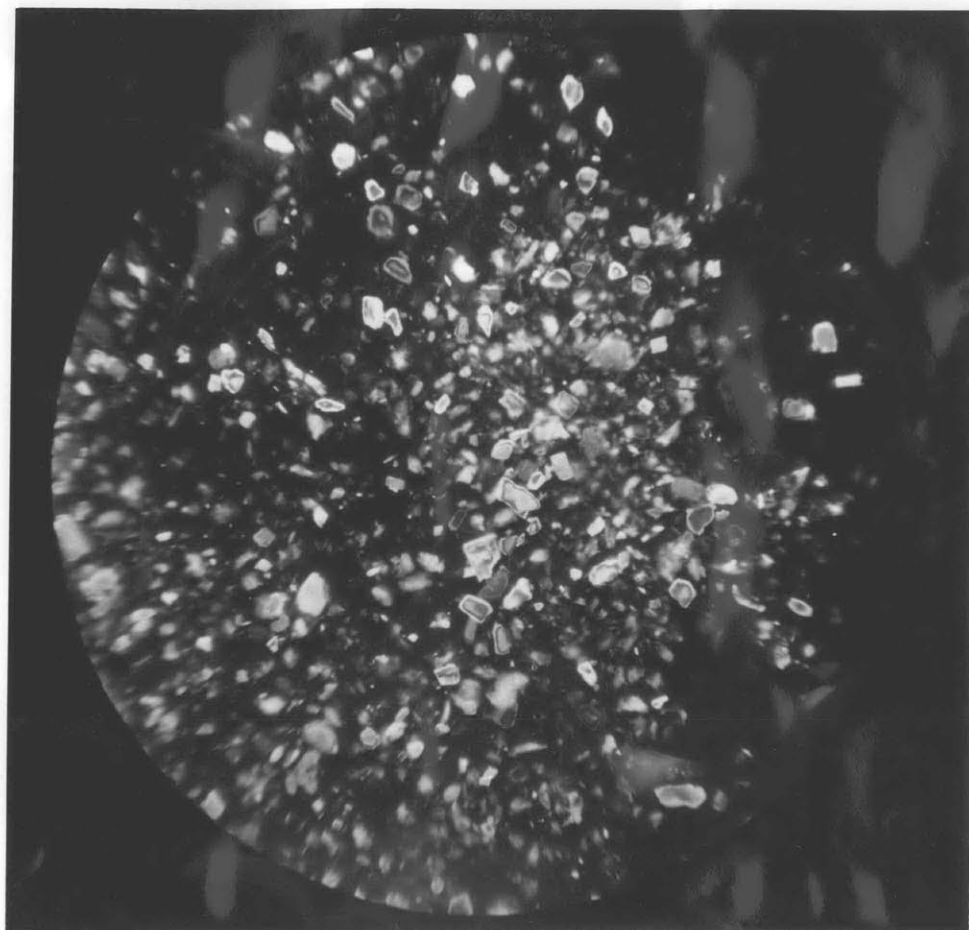


PLATE 8

POWDER SAMPLE OF "WATER-SHORT GYPSUM" (60X)

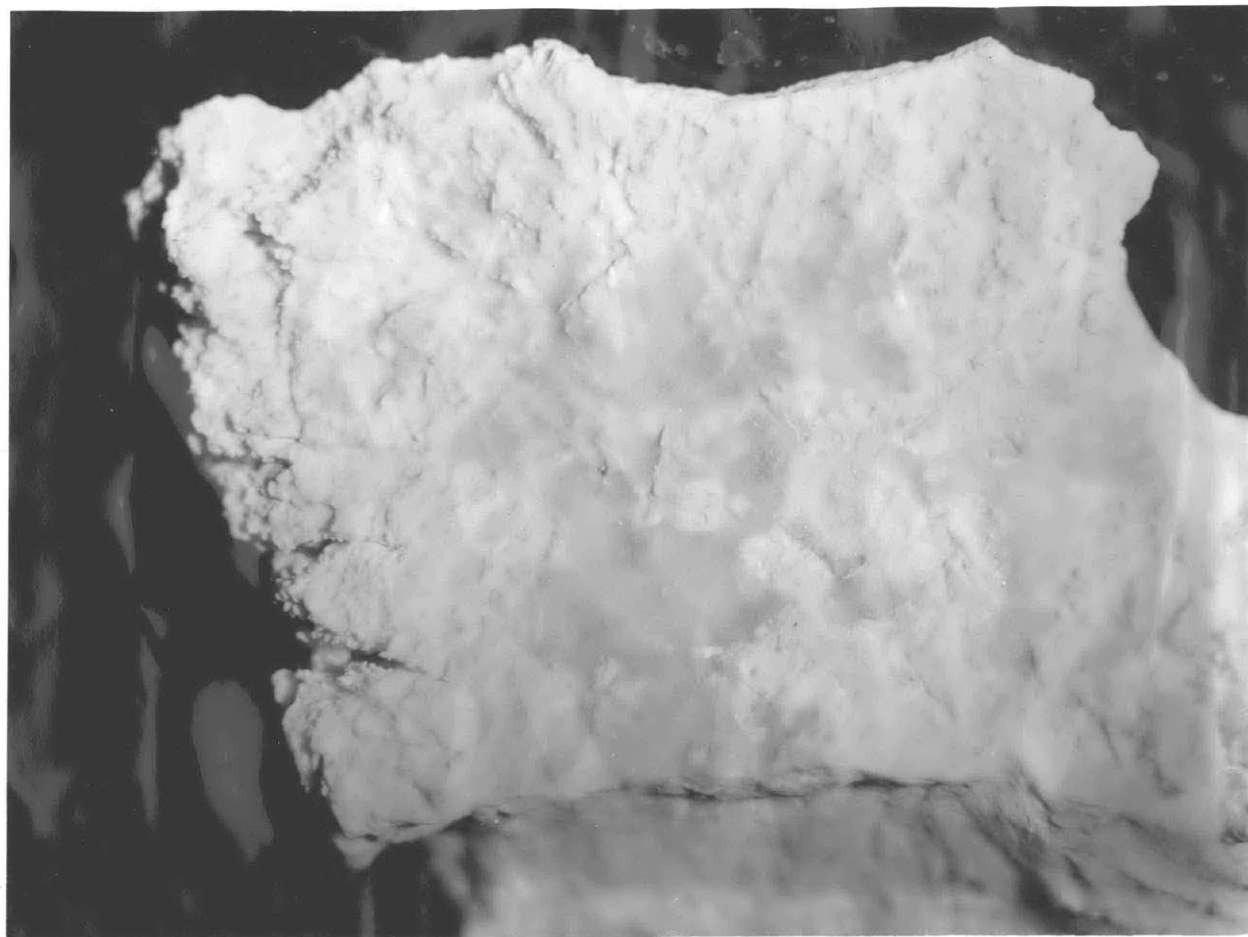


PLATE 9

ROCK SAMPLE OF "WATER-SHORT GYPSUM"

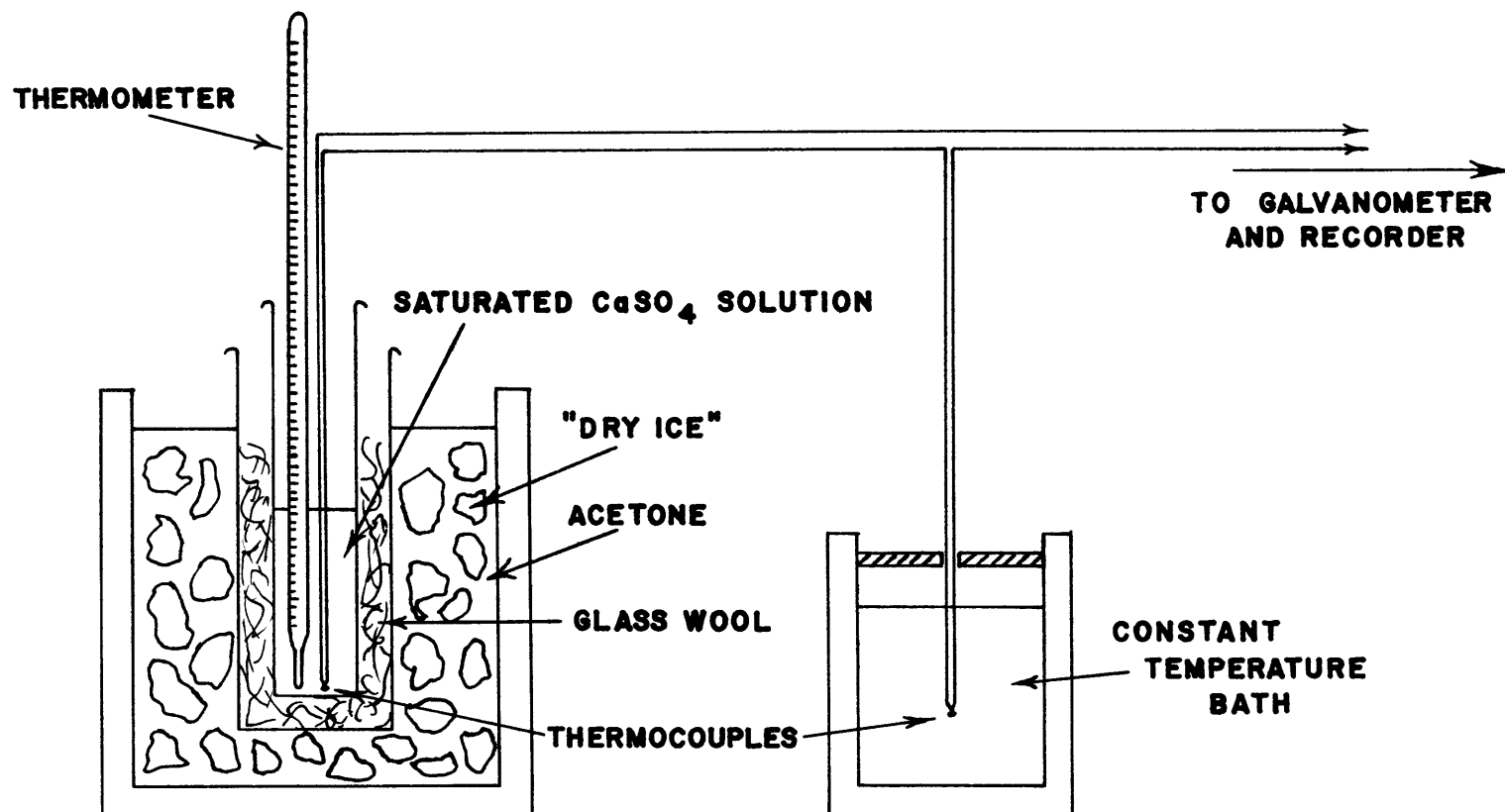
(2X)

than in the pure material. Inasmuch as the thermally inert portion of the "water-short gypsum" was shown to be anhydrite under the microscope and since no other compounds are indicated either under the microscope or in the thermograms, there is no reason to believe "water-short gypsum" consists of anything but a simple mixture of anhydrite and gypsum.

Geologically this can easily be explained by examining its mode of occurrence. In the gypsum beds exposed at the surface in Nova Scotia the most common form is in pockets or nodules up to the size of large boulders three or more feet across which are normally found imbedded in the pure gypsum. The bedding does not seem to be disturbed in the gypsum at these places and hence no reason to infer that the anhydrite-gypsum "boulders" were not formed in situ. Assuming that the bed was homogeneous at one time there are two possibilities: (1) the material was originally gypsum and the pockets or nodules have been partially converted to anhydrite, or (2) the material was originally anhydrite and these pockets are just remnants of the original material after conversion by a hydration process has taken place. The latter explanation is the more likely one to be correct.

CRYOHYDRIC POINT

The cryohydric point for a saturated aqueous solution of calcium sulphate was established by slowly cooling the



METHOD OF DETERMINING CRYOHYDRIC POINT

FIGURE 28.

pure liquid and carefully measuring its temperature at the freezing point. This was accomplished by first preparing a bath of acetone in a vacuum flask containing lumps of solid carbon dioxide. The latter has a melting point of -78.5°C , but the bath remained liquid since the acetone has a lower freezing point (-95°C). A large test tube was placed in the center of this bath and held in place, and into this tube another smaller test tube was inserted, the two being separated by an insulating layer of glass wool. The saturated calcium sulphate solution was poured into the inner tube and allowed to cool, the insulating layer slowing down the rate at which heat was extracted. This was done so as to keep the cooling process as even as possible and hence closer to equilibrium. As the solution cooled it was slowly stirred and its temperature recorded by means of a thermometer. An iron-constantin thermocouple attached to the lower end of the thermometer was connected in series with another thermocouple which was immersed in a constant temperature bath. The two couples were opposed to each other and connected to a recording galvanometer which kept a constant record of any differential thermal effects, and hence of any temperature changes within the solution. The galvanometer was calibrated every 0.1°C by reading the temperature on the thermometer and marking this point on the record. The combination of accurate temperature readings from the thermometer and continuous recording from the

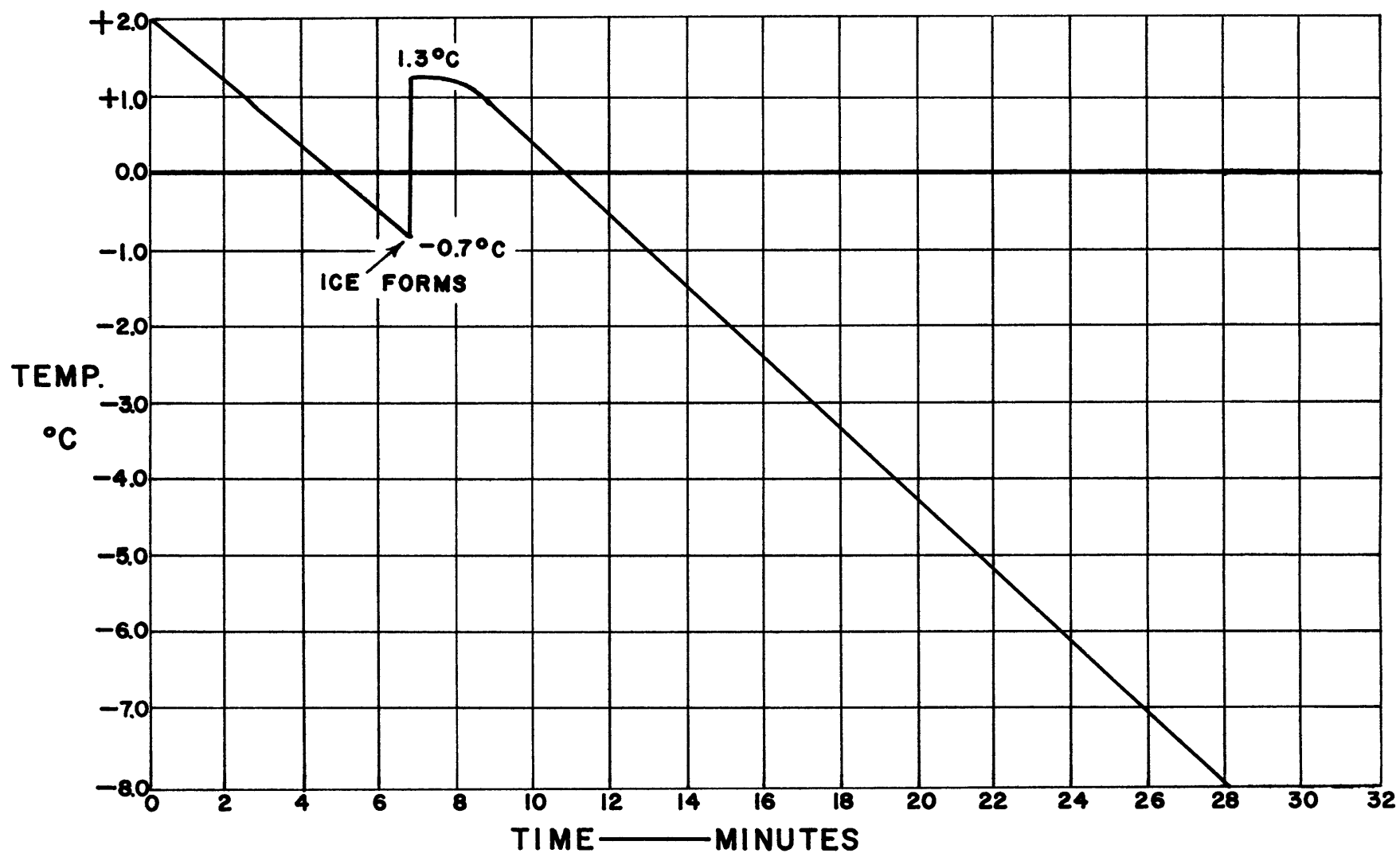


FIGURE 29.

thermocouple and galvanometer assured observations of all heat changes within the solution. A diagram of the layout of this equipment is shown in Figure 28.

The results of these determinations are shown as a single curve in Figure 29. It can easily be noticed that the temperature drops at an even rate until at -0.7°C there is a marked change in the behavior of the curve, indicating that heat is being rapidly absorbed, such as would be the case for crystallization from a liquid to a solid phase. Seven determinations of this point were made and they all agreed within 0.1°C . Simultaneous with the marked departure from the previous rate of temperature drop, the formation of ice crystals could readily be observed within the test tube. By definition, the cryohydric point was therefore established at $-0.7^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ for pure water saturated with calcium sulphate.

Some of the earlier determinations were made just by taking temperature readings at intervals, and not using the thermocouple for recording. The results were similar, although the freezing point could not be as closely observed. In most of the observations, as soon as freezing started the temperature of the liquid abruptly rose to about 1.3°C where it hovered for a short period of time and then dropped at a constant rate to about -10.0°C , at which point the experiment was considered completed. This rise of temperature is accounted for by the sharp absorption of heat from the newly formed solid phase by the remaining solution.

VACUUM DIFFERENTIAL THERMAL ANALYSIS

Early in this study a number of differential thermal analyses of selenite were prepared while the material was under a vacuum of about one millimeter of mercury, using equipment similar to that described by Whitehead⁶² and Breger. It was thought that under vacuum all the free water would be rapidly drawn off and would bring about greater differentiation between Peak A and Peak B in Figure 17. However, it had the opposite effect and tended to expand the base of the two endothermic peaks into one broad one, as shown in Figure 24. The peak indicating the first endotherm can still be distinguished, but shortly after reaching its maximum it runs into the peak of the second endotherm, which is then larger than the first one. This is the opposite to what happens when the sample is not under vacuum, where Peak A is always greater than Peak B. It can be noticed that the reactions start and end earlier when under vacuum. Unless the sample was tightly packed in the sample well, it would suddenly decrepitate at the height of the first peak, spraying the material completely out of the holder and ending the analysis at that point for lack of sample at the thermocouple. No observable effect was noticed when the sample was kept under vacuum for a period of one hour before heating was started. This would seem to indicate that it is difficult to rapidly dehydrate gypsum under vacuum unless it is near its dissociation temperature. Peak C remained the same,

whether the sample was under vacuum or exposed to normal room pressure.

CHAPTER III

GEOLOGIC APPLICATIONS

Although gypsum and anhydrite occur in connection with vein and other deposits, only the larger sedimentary types of deposits will be considered here. The majority of these are buried evaporite beds, although some are secondary deposits which have been altered from original limestones by sulphate solutions as described earlier.

Once calcium sulphate, either in the form of gypsum or anhydrite, has been precipitated and buried, it would be subjected to higher pressures, and changes in temperature. The former would tend to compact the mass of crystals and drive the connate waters out, decreasing the pore space. Ground water solutions in contact with such a deposit would tend to reach saturation with respect to calcium sulphate and a process of solution followed by recrystallization would slowly take place, governed by the prevailing temperature, pressure, and composition of the contacting solution, as described earlier. Since these solutions will have some access to the surface they will be under a hydrostatic head equal to the density of the solution (which will be very close to 1.0) times the depth of burial, whereas the solid material will be under a lithostatic head about 2.4 times

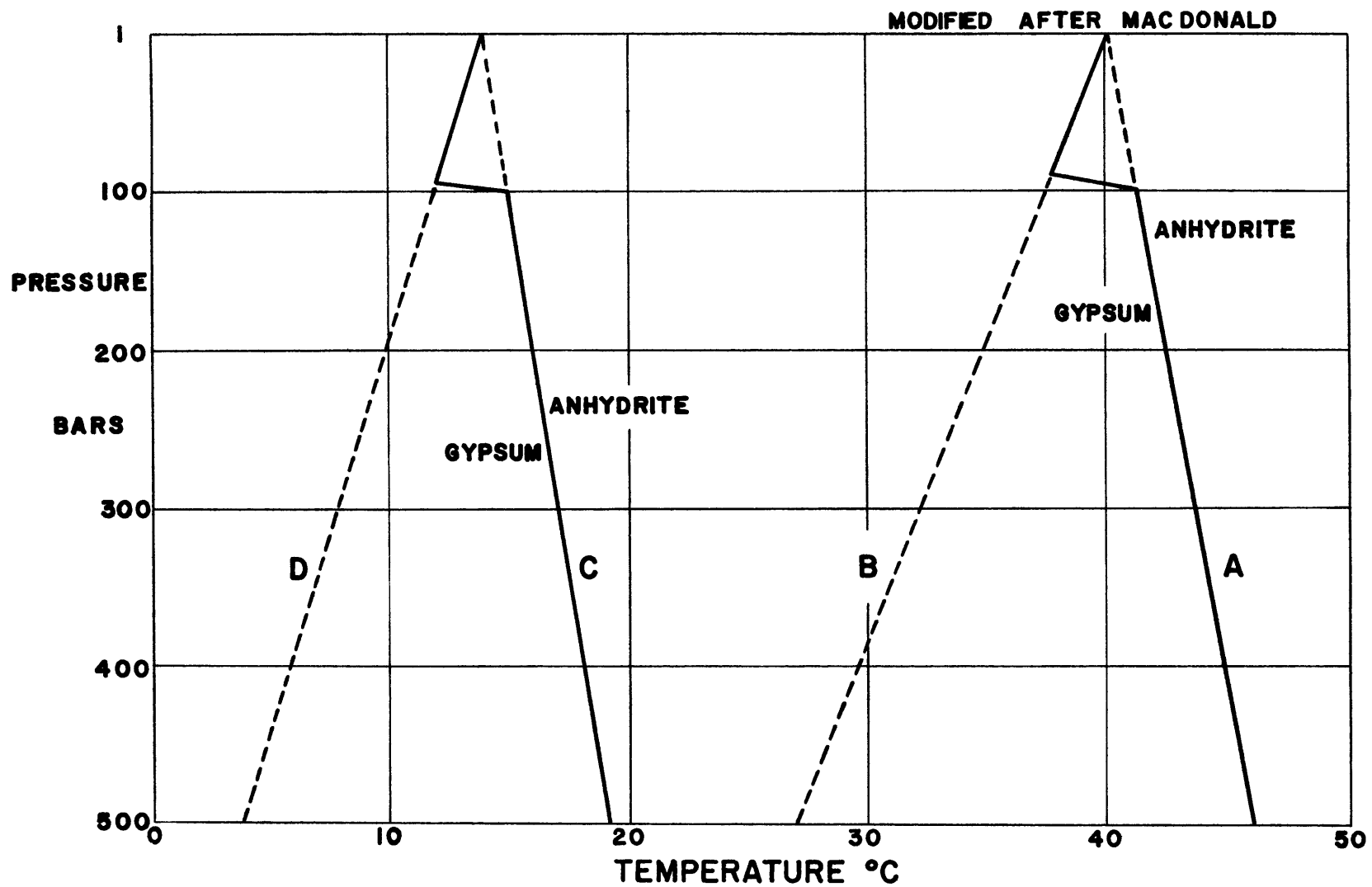


FIGURE 30.

this amount, depending on the density of the overlying rock. This difference in pressure will cause the transition temperature to vary according to Curve B on MacDonald's theoretically calculated plot³⁷ for a solution of pure water not containing dissolved salts other than calcium sulphate. However, when the depth of burial reaches the point where the pressure is great enough to cause flowage of the solid material the porosity, and particularly the permeability, will be greatly diminished. Any impermeable shalebeds overlying the material will also act as a barrier to escape of solutions to the surface, and Curve B on MacDonald's plot of variation of transition temperature with pressure will then no longer be valid or describe the true conditions.

Once the solution is sealed in with the gypsum or anhydrite after flowage has started, the hydrostatic pressure will increase and tend to approach the same value as the lithostatic pressure. This is shown as Curve A in Figure 30. The actual values at which this takes place are not known, although Griggs'²³ figure of 92 kg/cm^2 discussed earlier for gypsum can be used as an approximation. This would correspond to about 89 atmospheres, or approximately a depth of 1270 feet, assuming the average density of the overlying rock to be 2.4.

Assuming that since Curve A of Figure 6 has been shown to be experimentally correct, then curves B, C, and D are also

correct since they were calculated in the same manner, and it can be predicted how the transition temperature will vary if surrounded by a saturated sodium chloride solution. As with the curves for pure water, once the gypsum and anhydrite start flowing, the hydrostatic pressure will increase to the value of the lithostatic pressure and Curve D will swing over to join Curve C, as indicated in Figure 30. If the solution is not saturated with respect to sodium chloride, the transition curve will lie somewhere between Curve A and Curve C, depending on the actual concentration of the solution. These curves for intermediate concentrations can be calculated by MacDonald's method.

SOME CHARACTERISTICS OF GYPSUM DEPOSITS

There are a number of large gypsum deposits in Nova Scotia which are commercially exploited, the gypsum being used mainly as a building material. In quarrying the gypsum, large fresh faces are exposed and admirably suited for study and observation. The author spent only a short time observing these and collecting samples, but many of the field observations of others^{11,17,18} were also carefully noted. Much of the gypsum is a white, compact rock containing very thin beds of dark gray limestone, and is usually fairly pure, with an average of more than 95% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the quarried material. Although always crystalline, the gypsum is usually

fine-grained and consists of anhedral to euhedral crystals averaging about 0.1 mm in length. However, there can be considerable variation, and selenite crystals have been found by the author over a foot long. Some gypsum has a fibrous habit with the fibers parallel to one another and often forming a vein or fracture-filling of fairly constant thickness (up to about 3 cm); the fibers are perpendicular to the walls of the vein. The dark limestone often mottles the gypsum to give it a gray color and sometimes this may even appear brownish-gray. Often the gypsum is jointed and badly fractured, making it susceptible to infiltration by ground water solutions. In all known outcrops the surface material is gypsum and, where work has been done on the deposits, the underlying material has always been found to be anhydrite. Usually there is a much greater amount of the latter, such as that found in a hole drilled at Cape North where the gypsum was found to be only 25 feet thick as compared to the 275 feet of underlying anhydrite.¹⁷ The anhydrite is usually massive, finely crystalline, and somewhat bluish in color. The crystals usually vary in size from about 0.05 mm to 2 mm, with the larger ones showing the characteristic pseudocubic cleavage in thin sections. These may be present as lath-shaped, radiating crystals in spherulitic form. The anhydrite is often cut by irregular veins of very finely crystalline gypsum, and sometimes is found as lenses in the more massive gypsum. These are

interpreted by Goodman¹⁷ as being relics of former anhydrite beds before hydration to gypsum, or in some cases to be "fragments of the underlying anhydrite driven into the soft gypsum."

It is often difficult in the field to distinguish between gypsum and anhydrite when they are finely crystalline, and positive identification in many cases can only be assured after microscopic examination or some other means of analysis.

Sinkholes in gypsum are not uncommon, and in some areas completely pockmark the surface of the gypsum deposits. Dennen¹¹ has observed that these sinkholes penetrate through the gypsum layer but abruptly stop on the gypsum-anhydrite contact. They have not been observed in the anhydrite. Although they may be as deep as 20 feet or more, they are usually only about 3 feet or so wide. Often they are filled with "clay or earth," but are also sometimes found fairly empty of foreign matter and may have a thin cover of vegetation that deceives animals (and humans) who may break through this cover and fall into the sinkholes where they are trapped. Dennen has also observed that stream beds in these areas have their floors on the gypsum-anhydrite contact. Below 40°C anhydrite is more soluble than gypsum, and the lower the temperature, the greater is this difference in their solubilities. (At about 15°C anhydrite is about one and one half times as soluble as gypsum.) From this it might

seem strange that sinkholes appear in gypsum but not in anhydrite, and that the floors of the sinkholes and stream beds bottom on the anhydrite, but the explanation probably lies in the fact that this difference in solubility is offset by the considerably greater relative porosity of gypsum which makes it more susceptible to infiltration and solution by percolating ground water. Dennen has also noted that where overlain by a relatively impervious layer of clay, the thickness of the gypsum bed is less than in places where there is no such protective cover from water percolating downwards. Another observation was that the base of the layer of ground water rested on the upper surface of the anhydrite. This can be accounted for by the very low permeability of anhydrite in these areas.

STRUCTURE

In many cases, the contact between the gypsum and the underlying anhydrite has been observed to be parallel to the bedding, but the contrary is also found, that is, there are cases where there seems to be no relation between the bedding and the plane separating the gypsum and the anhydrite. The former would indicate a stratigraphic and structural relationship between the two, whereas the latter case shows that the gypsum was probably formed by straight surface hydration or, theoretically at least, that the underlying anhydrite was formed by dehydration of the gypsum---

this would be unlikely in the known surface deposits but it is very likely the case where there is a layer of salt just below the anhydrite. The salt would tend to saturate the surrounding ground water with sodium chloride, thereby considerably lowering the transition temperature and making anhydrite the stable phase for all temperatures near or above those expected at any reasonable depth. That such is the case has been shown theoretically, and is illustrated by a number of different examples in geologic deposits.

DRILL HOLE INFORMATION

The author had access to records of seven drill holes in Nova Scotia which went to depths of as much as 1400 feet. The holes passed through alternating beds of variegated shales, limestones, gypsum, halite, and anhydrite. In all but one of these drill holes, gypsum was never logged as being in direct contact with halite but always had a bed of anhydrite at least 12 feet thick separating the two evaporites. However, upon obtaining the actual core samples for the hole showing gypsum in direct contact with halite, and analyzing the material microscopically, it was found that the drill hole log was in error, and that the material was really anhydrite. It was pure white with a fine-grained sugary texture and could not be distinguished from gypsum in macroscopic examination alone.

Anhydrite always had some gypsum overlying it but the

DEPTH
IN
FEET

100

200

300

400

500

600

700

800

OVERBURDEN

GYPSUM

LIMESTONE

GYPSUM

ANHYDRITE

LIMESTONE

HOLE #1

OVERBURDEN

RED SHALE

Is

RED SHALE

Is

RED SHALE

GREY SHALE

RED SHALE

GREY SHALE

Is

RED SHALE

Is

GREY SHALE

GREY SHALE

GREY SHALE

RED
AND
GREY
SHALE

GYPSUM

ANHYDRITE

HALITE
TO
BOTTOM
1045'

HOLE #2

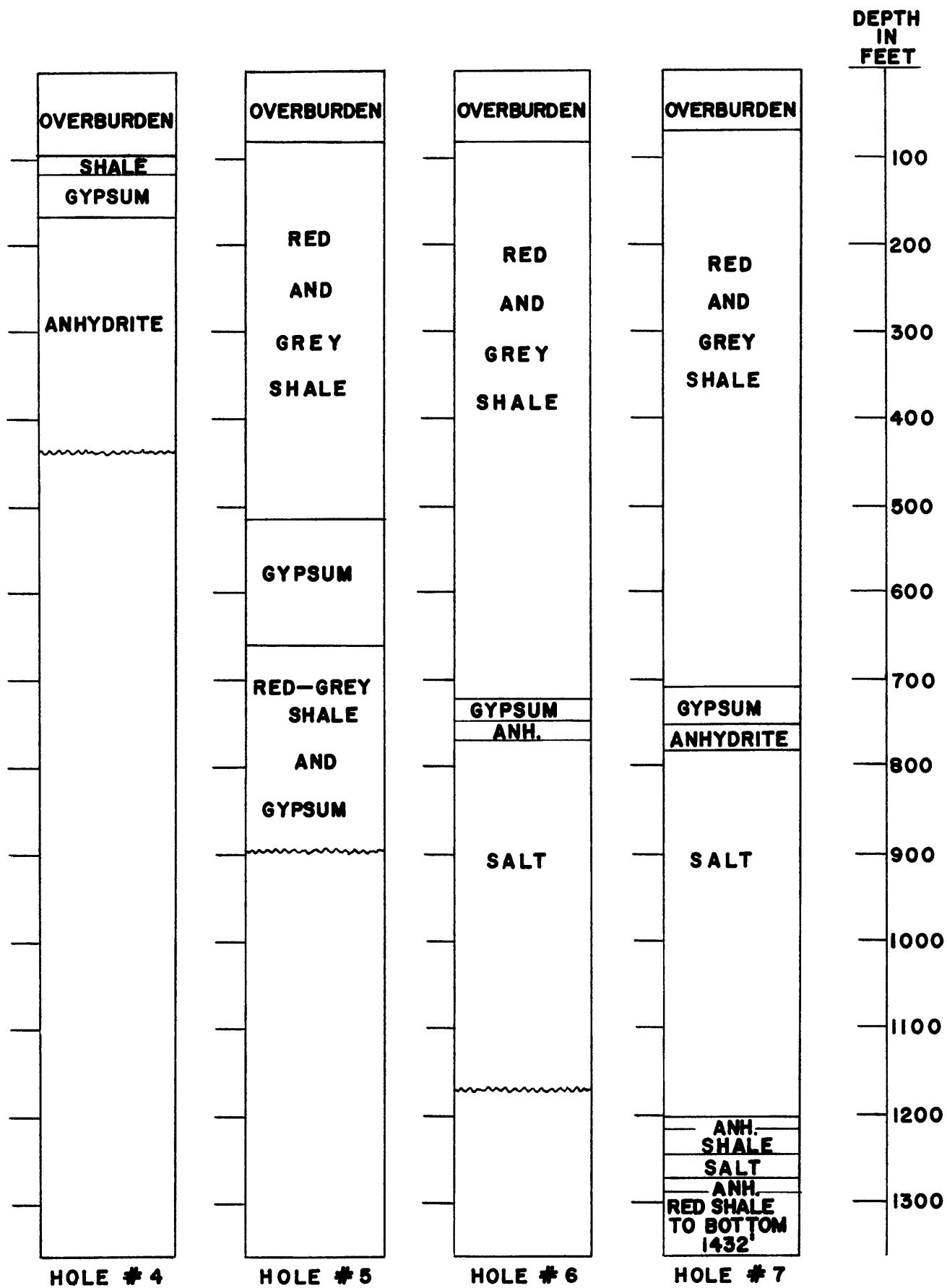
OVERBURDEN

RED
SHALE
WITH
GYPSUM
STRINGERSGYP.-ANHYD.
GREY SHALE

ANHYDRITE

HOLE #3

DRILL HOLE LOGS
FIGURE 31.



**DRILL HOLE LOGS
FIGURE 32.**

converse was not always true, that is, in the depth considered gypsum did not always have anhydrite beneath it, since the latter was completely absent in two of the holes. Also, the anhydrite did not necessarily have salt underlying it, although such was the case in two of the holes. An important point is that no bed of anhydrite was ever found at a higher level than the lowest gypsum bed in each hole. Figures 31 and 32 are logs of the seven holes.

As with many other similar evaporite deposits, the problem of determining the original order of deposition of the gypsum and anhydrite is difficult, if not impossible, to solve. If the complete history of temperature, depth of burial, and composition of ground water solutions was known, all the transition points could be determined and the true sequence of conversions could be traced. But since this is rarely, if ever, the case with any geologic deposit, assumptions have to be made and combined with the known facts to get some postulated picture of the events. In the present case, it is difficult to draw any positive conclusions as to the composition of the original material inasmuch as gypsum and anhydrite can readily replace each other under the proper conditions and are unstable with respect to each other when in contact with an aqueous solution except at unique points, some of which have already been specified. From the drill hole data mentioned above, however, several points can be made, namely: (1) it is likely that the anhydrite in contact

with the halite is stable only because of the high salinity of the contacting ground water solution; (2) unless the ground water in contact with the rest of the calcium sulphate is also highly charged with sodium chloride or other salts, which is unlikely, then gypsum is the stable phase for the expected temperature and pressure at these depths, and these deposits are probably very slowly being hydrated to gypsum, the rate being slow because of the very low porosity and permeability and the many relatively impervious shale beds above the deposits; (3) there is a level above which gypsum is the stable phase and below which anhydrite is the stable phase; the present level, even though it shows this relationship, may not be the true marker separating these stable zones (it probably lies at a greater depth), but might be indicative of regional uplift in the past, with the hydration of the anhydrite going on at an extremely slow rate.

In the deposits at Dingwall and at Little Narrows on Cape Breton Island, Nova Scotia, there is only a surface zone of gypsum overlying a much thicker sequence of anhydrite. Why the anhydrite has not completely hydrated to gypsum, even before it was brought to, or near, the surface, is unknown, for it is in a zone where it is unstable in contact with water. The explanation might lie in its low porosity and permeability as mentioned above, or the presence of highly saline solutions, which is less likely since there

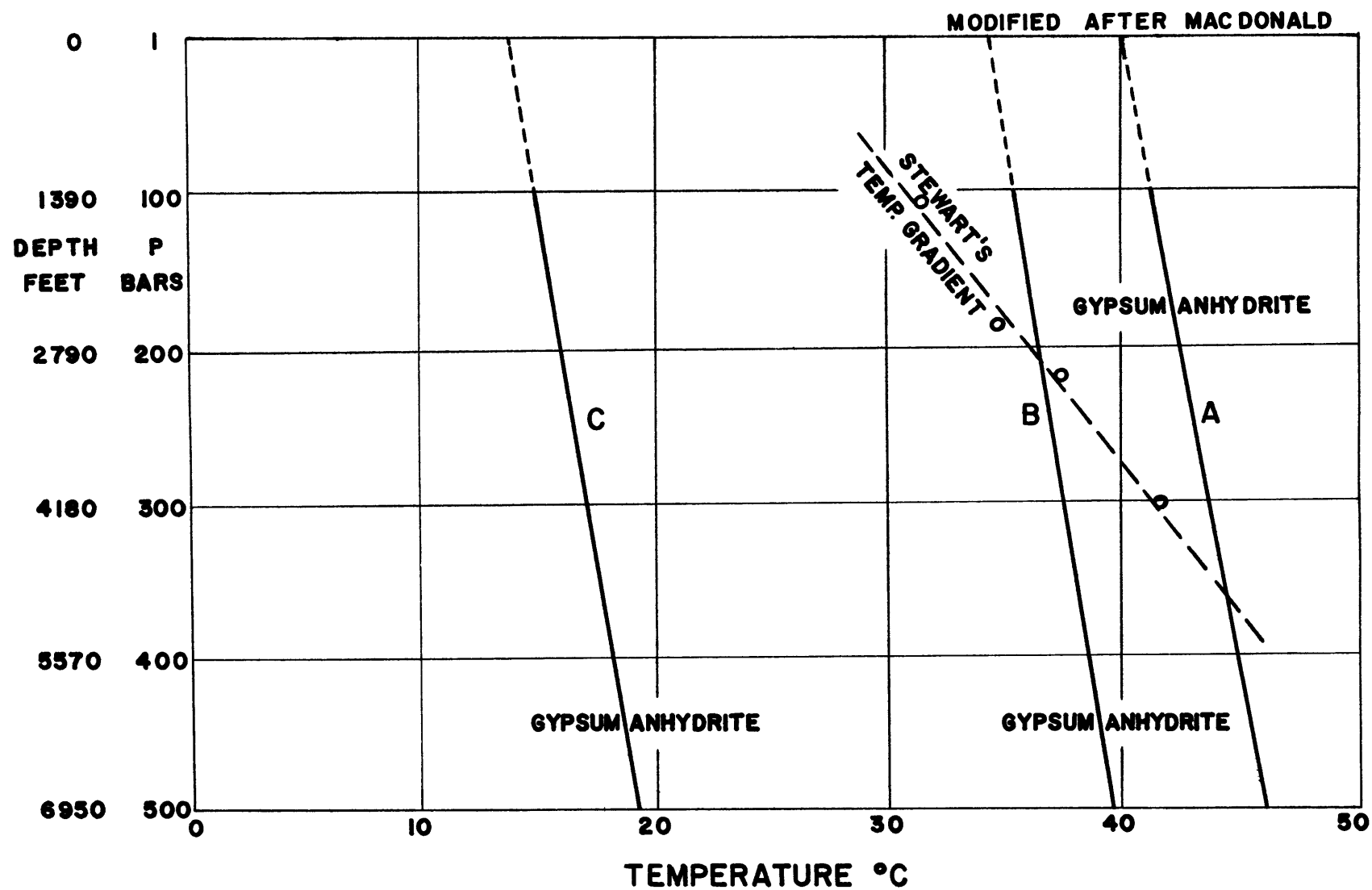


FIGURE 33.

is no indication of these in the areas mentioned.

In the discussion of the solubility of gypsum and anhydrite earlier in this paper, Posnjak's⁴⁵ work on their solubilities in different concentrations of sea water was mentioned. MacDonald³⁷ has shown from this and his own calculations that a chlorinity of about $65^{\circ}/_{\text{oo}}$ is reached (the chlorinity of normal sea water is about $19^{\circ}/_{\text{oo}}$) when sea water has evaporated down to the point where calcium sulphate is precipitated. This figure is 3.35 times the normal salinity of sea water, as shown by the intersection of lines on Posnjak's graph (Figure 5). If Posnjak's solubility relations are also true somewhat above the temperature at which he made his determinations (30°C), then 34°C is the calculated transition temperature, shown as Curve B in Figure 33. Above this, anhydrite is the stable phase; below it gypsum is the stable phase. Assuming a temperature below this figure, say between 20°C and 30°C , for the evaporating water within a lagoon or basin, gypsum would be deposited first, probably as very fine crystals. As they precipitate and form a consolidated deposit they would also trap much of the saline solution as connate water, and if no mixing takes place the salinity of the original water would continue increasing as more gypsum is deposited. If no disturbance takes place, such as fresh water being added to the basin, the evaporation would proceed to the point where the salinity is 4.8 times the normal salinity

AFTER MACDONALD

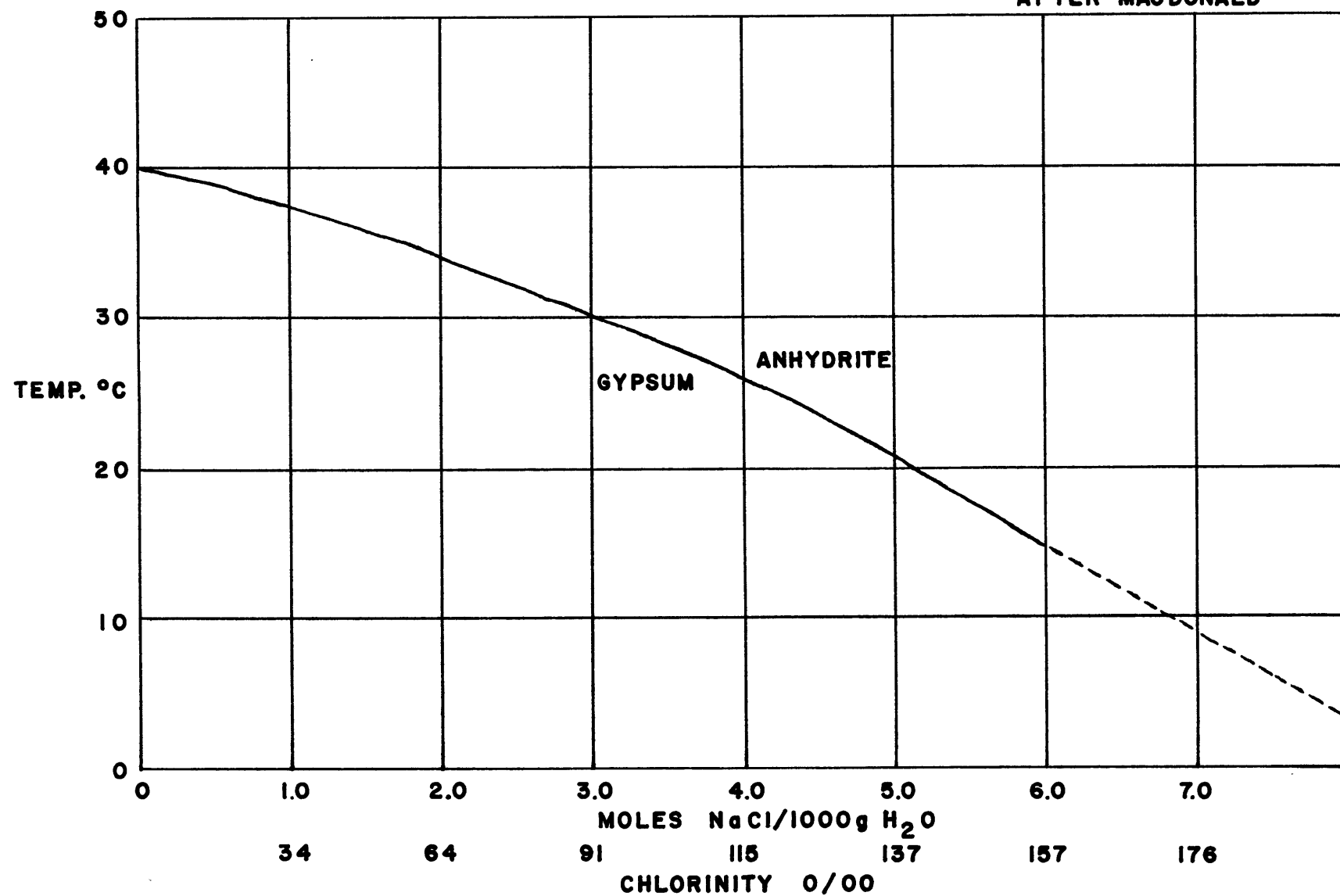


FIGURE 34.

of sea water, or a chlorinity of about $119^{\circ}/_{\text{oo}}$, and anhydrite will then become the stable phase and be precipitated, also trapping some solution as connate water. Continued evaporation would finally produce deposition of sodium chloride at a chlorinity of about $160^{\circ}/_{\text{oo}}$. For gypsum and sodium chloride to precipitate together in solutions of just calcium sulphate and sodium chloride, the temperature would have to be below 14°C . MacDonald points out that other salts in sea water would lower this temperature to 7°C , where the chlorinity would be $184^{\circ}/_{\text{oo}}$. See Figure 34.

This is an ideal situation, however, and is not too likely to occur, since the sequence of events can be quite easily interrupted, as indicated by the lack of salt upon many gypsum and anhydrite deposits. Also, diagenetic changes may take place, such as the conversion of gypsum to anhydrite after the former is buried and subjected to percolation of concentrated saline waters from above.

Stewart^{47,48,49} recently made a detailed petrographic study of Permian evaporite beds in England in which he worked out the present sequence of minerals, as found in drill hole cores. There are three main beds, which he describes as shown in Table IX. He has found evidence of the replacement of anhydrite by gypsum and then back to anhydrite again. There is also evidence of the replacement of anhydrite by gypsum and then to halite, anhydrite to

TABLE IX

<u>UPPER EVAPORITE BED</u>		
<u>DEPTH</u>	<u>ZONE</u>	<u>MINERALS AND DESCRIPTION</u>
3738	Zone of silty halite	Mostly pink, brown or colorless halite; some anhydrite, talc, sylvine, and carnallite.
3790	Zone of granular halite	Mostly pink granular halite; some anhydrite, magnesite, sylvine, and rinneite.
3834	Anhydrite zone	Mostly anhydrite; some subordinate magnesite, dolomite, and halite-anhydrite pseudomorphs after gypsum in upper part
3860		
<u>MIDDLE EVAPORITE BED</u>		
3910		Greenish-grey and red salt clay.
	Upper halite zone	Brown, red, and colourless halite, with greenish-grey clay.
3918	Halite-sylvine zone	Brown halite and some sylvine and clay.
3964	Halite zone	Brown, pink, red, and gray halite with anhydrite increasing in amount towards the bottom
4106	Halite-anhydrite zone	Anhydrite and halite; some anhydrite-halite pseudomorphs after gypsum.
4155	Anhydrite zone	Anhydrite with subordinate dolomite.
4196		Dolomite and dolomitic marl.
<u>LOWER EVAPORITE BED</u>		
4313	Halite-anhydrite zone	Halite and anhydrite.
4399	Upper anhydrite	Anhydrite with some halite.
4440	Polyhalite zone	Polyhalite, halite, and anhydrite.
4525	Lower anhydrite	Anhydrite with some halite
4773		

halite, and numerous other replacements with the remaining minerals. It should be noted that there was no gypsum found in the core samples, although pseudomorphs after gypsum were not uncommon and weathered samples exposed at the surface for some time were hydrated to gypsum. Repeated references are made to "early gypsum," and Stewart states that "gypsum was widespread as an early mineral," with the evidence suggesting that at least some of it was primary. Although at first he concluded that much of the basal anhydrite in each of the three evaporite beds was primary, later⁵⁰ he changed his opinion after finding numerous pseudomorphs of anhydrite after gypsum in these beds. "Above the basal anhydrite, halite-anhydrite zones, containing layers with pseudomorphs after gypsum, are interpreted as transition zones laid down when seasonal variations in temperature caused alternate deposition of primary gypsum with halite and primary anhydrite. Above these transition zones, the calcium sulphate was apparently deposited as anhydrite. All the early gypsum has since been converted to anhydrite and halite, perhaps partly by contemporaneous metasomatism by supernatant brines, and partly by increase of temperature due to burial beneath a thick cover of later sediment." Stewart explains the absence of gypsum by showing that the transition is well below the known temperatures, and therefore anhydrite is the stable phase for those depths, if a small amount of salt is present. Lees and Tait³⁵ measured

the temperatures in the drill holes and found them to be 107.1°F (41.6°C) at a depth of 4200 feet, 99.1°F (37.3°C) at a depth of 3000 feet, 94°F (34.4°C) at a depth of 2600 feet, and 88.6°F (31.4°C) at a depth of 1500 feet, thus giving a temperature gradient for these depths as 1°F (0.555°C) per 146 feet, which is a rather low figure. This gradient is plotted on Figure 33, along with the transition curves for calcium sulphate dissolved in pure water (Curve A), a saturated sodium chloride solution (Curve C), and a salt solution of intermediate concentration (Curve B) having a chlorinity of about 61‰, which is just about that of the concentration of sea water when it has just evaporated to the point where calcium sulphate begins to precipitate. These curves are for equal pressures acting on the solid and liquid phases, since it is assumed that at these depths the gypsum and anhydrite will flow sufficiently to seal off much of the pore space and raise the hydrostatic pressure up towards the same level as the lithostatic pressure. It is seen from the intersection of the measured temperature gradient with these curves that anhydrite is the stable phase for any aqueous solutions containing sodium chloride at a chlorinity of 61‰, or even at slightly lower concentrations. If the lithostatic pressure is higher than the hydrostatic pressure, then anhydrite would be the stable phase even for pure water, at these temperatures and depths, MacDonald having calculated the transition depth at

2500 feet. He also made a correlation between Stewart's interpretation of the sequence of anhydrite and halite beds and the anhydrite-gypsum equilibrium relations discussed in his paper on the thermodynamics of the transition. Stewart believed that there was "alternate deposition of gypsum-halite and anhydrite-halite," which would require temperatures of about 7°C during deposition, lower temperatures producing the first combination and higher temperatures producing the latter. MacDonald mentions another possibility, however, in which such low temperatures are not required. This first requires the deposition of halite and anhydrite after which "an influx of fresh water into the basin reduces the concentration of salts, halite is dissolved, and anhydrite is converted to gypsum." Later the gypsum is replaced by anhydrite and halite as the salt concentration increases again, and primary beds of anhydrite and halite are deposited above these, thus giving a final alternating sequence of anhydrite-after-gypsum-with-halite and primary-anhydrite-with-halite, which is that described by Stewart. The temperature of the sea water required for such a cycle could be as high as 34°C , above which no gypsum would be deposited.

SALT DOMES

MacDonald has correlated his calculations with data on gypsum and anhydrite deposits associated with salt domes. On Figure 6 he has plotted the temperature gradient over the

Grand Saline Dome in Van Zandt County, Texas, and has used this for estimating the depths of the transition temperatures for other deposits. In pure water, assuming different pressures acting on the solid and liquid phases, 1820 feet is the depth below which anhydrite is the stable phase. However, as pointed out earlier, if the deposit is buried over 1270 feet it might start deforming by plastic flow. This would then lower the transition depth, corresponding to the above temperature gradient, to 2600 feet. Saline waters would tend to raise this depth till it intersects the surface, and then only anhydrite would be stable. Goldman¹⁶ did a considerable amount of detailed petrographic work on the gypsum and anhydrite in the cap rock of Sulphur Salt Dome after examining numerous thin sections made from diamond cores. The cap rock is about 1100 feet thick, and the deeper part in contact with the underlying halite consists of anhydrite that seems to have replaced gypsum, although it is difficult to really prove many of the changes, either from gypsum to anhydrite or vice versa. Anhydrite is predominant from 1183 feet down, however, and MacDonald places this as the estimated transition level, although there are some reports of occurrences of gypsum as deep as 2080 feet. Assuming a salinity of 61⁰/₀₀, which would be about that of sea water at the point where calcium sulphate first begins to precipitate, MacDonald shows that the temperature-depth curve would be intersected by the

temperature-gradient curve at about 1300 feet for unequal liquid and solid pressures. This would be about 1800 feet for equal pressures, as shown in Figure 6. Both figures are within the limits of the "uncertainty in temperature gradients and groundwater composition." MacDonald also points out the fact noted earlier that gypsum is not found in contact with beds of sodium chloride but is separated by a layer of anhydrite, which is the case for this and other salt dome caps.

BIOGRAPHY

The author was born on April 12, 1929, in New York City where he received all his early education. After graduation from Stuyvesant High School he spent his first half year of college in early 1946 at the Colorado School of Mines in Golden, Colorado, where he majored in Geological Engineering. The next half year he was employed as a Geologic Field Assistant with the Metals Branch, and later the Engineering Branch, of the United States Geological Survey in southwestern Colorado. In 1947 he returned to academic studies at The Johns Hopkins University in Baltimore, Maryland, where he majored in Geology, and received his Bachelor of Arts degree upon graduation in June 1950.

In September 1950 he entered the Massachusetts Institute of Technology, and received the degree of Doctor of Philosophy in Geology in September 1954. At M.I.T. he was awarded a Graduate Scholarship, and three Research Assistantships sponsored by the National Lime Association. During the summers from 1947 to 1952 he worked with the Engineering Branch of the Geological Survey in North Dakota, Washington, and Montana, twice with the Alaskan Branch in Alaska, and with the Geophysics Branch in Minnesota, Maine, and Washington, D. C. Part of the summer of 1953 was spent collecting material for this thesis in Nova Scotia on a Grant-in-Aid sponsored by the Nova Scotia Research Foundation.

Another Grant-in-Aid was used to support the experimental portion of the thesis. He is the co-author of several publications and maps distributed by the Geological Survey, and several papers connected with his work on the National Lime Association Fellowship.

He and his wife Agnes were married in January 1951 and had their first child, Richard Alan, in July 1953. At present, the author is connected with the Gulf Oil Corporation in Texas on a petroleum exploration program.

ACKNOWLEDGMENTS

The author wishes to extend his thanks to all of those who offered their assistance in the carrying out of the work for this thesis. He particularly wishes to gratefully acknowledge the continued direction and encouragement given him by Professor Walter L. Whitehead, who gave the original suggestion for undertaking a study of the gypsum problem and supplied the title for this thesis.

Thanks are also due Professor Gordon J. F. MacDonald and Dr. Paul L. Cloke for technical advice, Professor Harold W. Fairbairn for use of the pressure apparatus in carrying out the experiments, Professor William H. Dennen, who provided field notes of his observations on gypsum deposits, and Lewis H. King for assistance in using the differential thermal analyzer. Appreciation is expressed to John A. Solo of the Geology Machine Shop, who helped design and then built the special high pressure bombs.

In Nova Scotia, Professor Donald J. MacNeil of Saint Francis Xavier University generously made available the drill hole logs from South Side Harbor, and was most helpful in providing suggestions for travelling around the Province. His staff at the Nova Scotia Centre for Geological Sciences furnished help in obtaining core samples of gypsum and anhydrite. I would like to thank Dr. Nordau R. Goodman of Dalhousie University in Halifax for providing data and suggestions for the experimental work. The hospitality offered

by Mr. C. B. Hume, the plant manager of the National Gypsum Company Ltd. at Dingwall, Mr. Reginald Charlick, the manager of the Victoria Gypsum Company Ltd. at Little Narrows, and the helpful co-operation of their foremen and employees was greatly appreciated.

Field expenses and funds for the experimental work were provided by several Grants-in-Aid from the Nova Scotia Research Foundation. Financial assistance for graduate study was partly furnished by fellowships from the National Lime Association.

Finally, the author wishes to express his grateful thanks to his wife, Agnes Ann Rolnick, for her constant encouragement and for typing and proofreading some of the final copies of this thesis.

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